

CATION EXCHANGE

in

SOILS

by
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Dedication

This monograph is dedicated to Mr. S. Melvin Brown of the Citrus Experiment Station of the University of California. For a period of more than 20 years, Mr. Brown collaborated with the writer in his researches on cation exchange. His untiring cooperation made it possible for the writer to gain first-hand insight into many aspects of cation exchange. Much unpublished data which Mr. Brown's cooperation made possible have been consulted in the course of writing this manuscript.

GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the

artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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Preface

Soon after the discovery was made in 1850 that soils have the property of exchanging calcium, and magnesium to a lesser extent, for ammonium and potassium, the term *base exchange* began to be applied to the process. At that time it was not known that the hydrogen ion can participate in the exchange reaction. In fact, the very existence of the hydrogen ion was unknown. It was many years after the publication of Arrhenius' electrolytic dissociation theory in 1887 that soil scientists began to apply this concept to soil reaction. But long after it became known that the hydrogen ion may take part in the exchange reaction, the use of the expression *base exchange* was continued, even where the reference was to exchange between metallic cations and hydrogen ions. In fact, the term *base exchange* is widely used in present day literature on soils and other kinds of material. In view of the importance of the hydrogen ion in the exchange process, and the fact that cation exchange is similar in principle, whether the exchange is between metallic cations or whether hydrogen ions or some organic cations exchange with metallic cations, the term *cation exchange* is the more appropriate. However, in deference to historical usage, *base exchange* will be used in the discussion of the historical development of the subject. In other parts of this monograph, the more correct term will, for the most part, be adhered to, but wherever used, *base exchange* denotes *cation exchange*.

Wiegner (1912) used the German word "*eintausch*" as referring to the taking up of an ion from solution by a solid through exchange, "*austausch*" as the release of an ion from a solid by exchange, and "*umtausch*" as referring simply to the process of exchange. The words *adsorb*, *replace*, and *exchange* are the approximate English equivalents of these German words.

It follows, then, that ordinarily cation exchange is a process involving a solution and one or more solids. Under certain circumstances, which will be discussed in Chapter 7, cation exchange may take place between two solids, the solution phase not being directly involved. To do so, the solids must be in close proximity and then

the process has been called *contact exchange*. The system most commonly dealt with consists of a solid phase in equilibrium with a liquid phase. The exchangeable cations are held on or near the surface of the solid. In most ion exchange reactions the amount and over-all chemical composition of the solid phase are not greatly altered. Thus the process is roughly distinguished from ordinary chemical reactions involving solids and solutions.

In its usual connotation, cation exchange in soils refers to that process in which some cation of the soil exchanges with a cation of a solution. Usually the reference is to the change which the soil undergoes, but the solution always undergoes a reciprocal change. The solution loses cations to the soil and gains an equivalent amount of cations from the soil. As with all chemical processes, cation exchange must be stoichiometric, but soils commonly contain soluble substances as well as exchangeable cations. For this reason it is not always easy to distinguish the exchange process from solution processes.

The property of exchanging cations with solutions is by no means confined to soils. Many other substances have similar property, for example, soaps, proteins, certain resins, and many other organic substances. Cation exchange is directly involved in geological processes, particularly in the weathering of rocks and minerals, and industrial uses for the exchange process are multiplying rapidly. Ion exchange (both cation and anion) is an important aspect of surface chemistry. The principles governing the process seem to be similar with all kinds of material. As will be shown later, the exchangeable cations are mainly held by electrostatic attraction. However, in some cases covalent bonds are probably involved.

The chemical and physical properties of the soil may be profoundly influenced by cation exchange. Perhaps no other aspect of the soil has such far-reaching importance. In the early development of the subject, scientific and practical interest was primarily centered on the use of potassium and ammonium fertilizers. Soil scientists, from the time of Way to the present, have been impressed by the fact that potassium and ammonium, applied as fertilizers, are taken up by the soil and held against the leaching action of rains or irrigation water, but at the same time they remain in a condition in which they can be utilized by growing plants. This fact is still of great interest to soil scientists and also to producers

of commercial fertilizers, as well as practical farmers. Indeed, this is perhaps the most widely known example of cation exchange.

During recent years other aspects of cation exchange have been recognized, and these have assumed considerable importance. Through studies on cation exchange, soil acidity has come to be much better understood, and practical means for its control have been developed. The relation between cation exchange and the availability of plant nutrients in general is now recognized. Cation exchange has an important bearing on the physical and microbiological processes of soils. It is probably involved to an important degree in soil formation and soil erosion.

Not until the significance of cation exchange was recognized, particularly in regard to the relations of the sodium ion, was it possible to understand certain important properties of alkali soils. On the basis of cation-exchange investigations, effective methods for the reclamation of alkali soils have been worked out. Thanks to our knowledge of the process, effective and thoroughly practical methods have been developed for the improvement and complete conversion of barren alkali lands, not only into highly productive soil, but also into a condition that is essentially the same as that of productive soils in general. Before the cation-exchange relationships of alkali soils were appreciated, great difficulty had been experienced in the reclamation and profitable utilization of alkali soils.

It is not necessary to review all of the numerous papers on cation exchange in this monograph. Only those of chief historic interest and those which reveal the evolutionary development of the subject will be discussed. Literally hundreds of papers have been published, all but a few of which have been read by the author, and these are probably of little importance. Many of the published papers are of purely local interest and throw no light on general principles. At most, they have served merely to confirm the conclusions already drawn by others. The reader who is interested in a more comprehensive biographical review of the subject is referred to sections in Blanck's "Handbuch der Bodenlehre", Volume VIII, by Gehring and Kappen.

From the time of the discovery of cation exchange (1850) to the beginning of Wiegner's investigations (1912), the exchange process was almost universally referred to as *absorption*. Subsequently the exchangeable cations have more commonly been designated as *ad-*

sorbed. In the historical discussions of the period 1850 to 1912 the usage in this monograph will follow that of the authors of this period. In other parts of this book, the cations in question are referred to as exchangeable or adsorbed.

As is well known, the word adsorb is widely used in reference to the condensation of molecules on the surface of solids by van der Waals forces. On the other hand, the cations referred to herein are held by electrostatic attraction. However, these cations are located exterior to the surface of the particles or on surfaces of internal channels, cavities, etc. They can therefore be said to be *adsorbed*. The condensed molecules referred to above can be removed without altering the solid, while the exchangeable cations can be removed only by exchange for some other cation of equivalent charge. With the exception of water and the uptake of nutrients by plants, the nouns *absorption* and *adsorption* and the corresponding verbs and adjectives as used herein always refer to exchange.

Throughout this discussion the primary emphasis will be placed on principles rather than on applications. For this reason but little will be said about techniques or practical procedures that must be followed in their application. As with science in general, when the principles are thoroughly understood, ways and means of utilizing the same can usually be found readily, and without an understanding of principles, the procedures are likely to be empirical.

However, it is important to emphasize two points at the outset: (1) We cannot say as yet that the essential principles are fully understood in all their ramifications. Perhaps this will remain true for a long time, since knowledge commonly opens new problems. (2) We are not justified in proposing dogmatic explanations of all the principles which now appear to be certain. In this connection the statements of the late G. N. Lewis have an important application. In the preface to his monograph on "Valence and the Structure of Atoms and Molecules", he pointed out that it was his purpose "to record a momentary phase of current thought, which may at any instant change with kaleidoscopic abruptness. It is therefore not unlikely that some of the things said in this book may have to be unsaid, but I trust that these may be matters of detail rather than essence."*

* Lewis, G. N., "Valence and the Structure of Atoms and Molecules," New York, Chemical Catalog Co. (Reinhold Publishing Corp.), 1923.

It should be understood that the explanations of cation exchange suggested herein are largely tentative. Many of them will probably require revision as new information becomes available.

Finally, it should be emphasized that cation exchange, although important, is not the only property of the soil of significance to the soil scientist and to the agronomist.

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Berkeley, California
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Chapter 1

History of Cation Exchange

Discovery

The discovery that soils have the power of exchanging cations with solutions was the outgrowth of observations dating back into the remote past. The fact that liquid manures become decolorized and deodorized upon filtration through soil has been known for centuries. Likewise it has long been known that the absorptive power of the soil is not confined to colored and putrid substances, but also includes ammoniacal fumes. The fact that manure heaps give off gaseous ammonia was observed long ago, and when, in the early part of the 19th century, it became known that living plants require nitrogen for their growth, it was to be expected that soil scientists would become interested in the ammonia-absorbing power of the soil.

Another fact also played a part in the early development of the subject, namely, the claim, repeatedly made in the 18th and 19th centuries, that sea water is made fresh by seeping through beds of sand. The early idea was that the dissolved salts are preferentially adsorbed by the sand grains. That this idea was probably the outgrowth of faulty observations, will become apparent as this discussion proceeds.

Being well aware that soils have the power of absorbing gaseous ammonia, Thompson (1850) attempted to determine (1) whether ammonia, once absorbed by soil, can be leached out by rains, (2) whether soils differ one from another in their ammonia-absorbing power, and (3) whether this power includes the absorption of ammonia in the form of ammonium sulfate, which was then coming into use as a nitrogenous fertilizer. Thompson's experiments were begun in 1845, but were not published until 1850, when Way had already conducted a much more thorough investigation of the subject.

In his first experiment, Thompson analyzed the leachates obtained by percolating water, equivalent to a 3-inch rain, through

short columns of sandy loam soil to which 0.64 gram of $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{CO}_3$ had been added. The leachates were found to contain the following:

<i>Tube A</i> $(\text{NH}_4)_2\text{SO}_4$		<i>Tube B</i> $(\text{NH}_4)_2\text{CO}_3$	
CaSO_4	0.256 gm	CaSO_4	0.064 gm
$(\text{NH}_4)_2\text{SO}_4$	0.154 gm	NH_4Cl	0.083 gm
Other sulfates	0.038 gm	$(\text{NH}_4)_2\text{SO}_4$	

The fact that a considerable part of the added $(\text{NH}_4)_2\text{SO}_4$ was converted into CaSO_4 by passage through the soil suggested to Thompson that NH_4 -absorption is associated in some way with lime in the soil. It will be noted that only about one-fourth of the added $(\text{NH}_4)_2\text{SO}_4$ was recovered in the leachate and only about one-eighth of the NH_4 added as $(\text{NH}_4)_2\text{CO}_3$.

In Thompson's second experiment, solutions containing the same amount of $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{CO}_3$ were percolated through similar columns of soil. The percolates were poured back on the soil and allowed to drain through a second time, after which the soil was leached with water as in the first experiment. Analysis of the combined leachates showed the following:

<i>Tube C</i> $(\text{NH}_4)_2\text{SO}_4$		<i>Tube D</i> $(\text{NH}_4)_2\text{CO}_3$	
CaSO_4	0.403 gm	CaSO_4	0.006 gm
MgCl_2	0.064 gm	CaCl_2	0.016 gm
		MgCl_2	

Thus, the soil absorbed all the NH_4 added as either $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{CO}_3$.

Similar results were obtained with a highly organic soil. With a clay soil the first drops of percolate were entirely free from NH_4 .

In his final experiment Thompson added NaCl to the soil followed by leaching with water. On the basis of Cl determination, he concluded that sodium is not absorbed by the soil. Although his previous experiments showed that NH_4 of the solution exchanged with Ca of the soil, this last experiment reveals that Thompson failed to appreciate the significance of his results, for the same amount of Cl will be present in the leachate irrespective of cation exchange owing to the fact that Cl is usually not appreciably absorbed by soil.

Thompson discussed his experiments with Way, who was then consulting chemist of the Royal Agricultural Society, and who at once appreciated the significance of the results. Way immediately

took up extensive investigation of the absorption process. In his first paper, published in 1850, Way reported a large number of experiments. The following conclusions were drawn:

(1) The cations of a neutral salt solution are absorbed by the soil, and this is accomplished by the displacement of an equivalent amount of Ca from the soil, but the anion of the salt remains in solution, provided an insoluble Ca salt is not formed. Thus by passage through the soil, $(\text{NH}_4)_2\text{SO}_4$ is converted into CaSO_4 ; NH_4Cl is converted into CaCl_2 ; but $(\text{NH}_4)_3\text{PO}_4$ is converted into $\text{Ca}_3(\text{PO}_4)_2$, in which case both the cation and anion disappear from the solution.

(2) The absorption is not caused by sand, organic matter, CaCO_3 , or free alumina, but by the clay fraction of the soil.

(3) The absorptive power of the soil may be reduced by preheating the sample, but is not completely destroyed unless it is heated to a high temperature.

(4) The rate of absorption is rapid, like the reaction between an acid and an alkali.

(5) Ammonium hydroxide and $(\text{NH}_4)_2\text{CO}_3$ are absorbed by the soil in their entirety, practically no exchange of cation taking place.

(6) The base-exchange power of the soil is not restricted to NH_4 , but also includes K, Na and Mg. However, if any of these is applied as the hydroxide or carbonate, the base is absorbed without exchange.

(7) Calcium added as a solution of the sulfate, chloride or nitrate passes through the soil unchanged, but $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{HCO}_3)_2$ are absorbed in their entirety, like alkaline compounds of other cations.

(8) The NH_4 -absorbing power of the soil increases with the concentration of the solution, and also as the ratio of solution to soil is increased.

(9) The base-absorptive power of the soil is irreversible.

Among Way's conclusions, (1), (3), (4) and (8) have stood the test of time to a remarkable degree and a substantial part of conclusions (2) and (6) have been verified by many soil scientists. On the other hand, conclusions (5), (7) and (9) were for the most part erroneous.

The conclusion that organic matter takes no part in the exchange process was certainly erroneous. This error probably arose from the fact that the soil used in Way's experiments was low in organic matter.

Although Ca is commonly the chief exchangeable cation of soils, we now know that Ca ions are by no means the only exchangeable cations present. Some soils, which incidentally are highly productive, contain as much exchangeable Mg as exchangeable Ca. A similar relation between exchangeable Na and Ca ions is a frequent occurrence in the alkali soils of arid climates, and practically all soils contain at least small amounts of exchangeable cations other than Ca ions.

At the time of Way's investigations, the fact that H ions can also take part in exchange reactions was unknown, and this largely accounts for his conclusion that alkaline compounds are absorbed without exchange.

Way's most important error was his conclusion that the exchange of cations is irreversible. This error can be accounted for by the fact that the principle of chemical equilibrium was not well established at that time. As we shall see, the cation exchange reaction is largely reversible in all known cases, and the exchange between Ca, Na and NH_4 ions is usually completely reversible.

In 1852 Way published his second paper, the primary purpose of which was to show just what kind of substance is responsible for the absorption and exchange of cations. Having concluded in his first paper that the exchange of bases was caused by the clay material of the soil, he attempted to determine more specifically the substance involved. Since the clay materials of most soils are largely silicates, Way first prepared simple Ca silicate, but this substance failed to absorb NH_4 . Complex double silicate of Al and Na was then prepared by bringing together solutions of alum and sodium silicate. The resulting precipitate was filtered out, washed free from soluble Na and dried. Upon digesting this material with NH_4Cl , he found that considerable NH_4 was absorbed. Double silicate was then prepared in another way, namely, by dissolving $\text{Al}(\text{OH})_3$ in NaOH solution and then adding sodium silicate. The water-free composition of the precipitate thus obtained was:

	%
SiO_2	52.42
Al_2O_3	29.68
Na_2O	17.91

Upon digesting this substance with an excess of lime water, Na

was released and a substance was formed having the following composition:

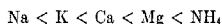
	%
SiO ₂	53.33
Al ₂ O ₃	30.21
CaO	16.46

Way pointed out that K aluminosilicate can be prepared either by using K silicate instead of Na silicate in the preparation of the precipitate, or by digesting Ca or Na aluminosilicate with K₂SO₄ or KCl. The substance prepared by the latter method had the following composition:

	%
SiO ₂	47.97
Al ₂ O ₃	27.17
K ₂ O	24.86

When any one of the foregoing aluminosilicates is digested with a solution of NH₄Cl or (NH₄)₂SO₄, Way claimed that NH₄ replaced Ca, Na or K with the formation of the corresponding NH₄ aluminosilicate.

The order of the replacing power of the common bases, as given by Way, was:



He pointed out that any one of these bases is able to replace any of those to its left in the above list, but "the reverse of this action can not occur and therefore the double silicate of Al and NH₄ can not be decomposed by any neutral salt of the other alkalies." Although this conclusion is in harmony with the idea that the exchange process is irreversible, it is nevertheless strange that it should have been drawn, since, as noted already, Way showed that K ions can replace Ca ions from both soil and artificial precipitate.

Being impressed with the fact that soils have pronounced ammonia-absorbing power, Way concluded that nature takes advantage of this power as a means of assuring a supply of nitrogen for plants. The fact that the absorptive power of artificial silicates is destroyed by heating the sample to a high temperature, suggested an explanation for the feeble absorptive power of igneous silicates, namely, that the aluminosilicates must be hydrated. Some sub-

stance quite similar to his artificial precipitates was thought to be responsible for the cation-exchange power of natural soils.

Despite the error with respect to the reversibility of the exchange process, the failure to recognize the role of H ions and organic matter and the emphasis on artificial precipitates, Way's investigations on base exchange were much the most important of the 19th century and of the first decade of the 20th century.

Early Development of the Subject

Liebig (1855) devoted his first paper on this subject to criticism of Way's paper on artificial silicates. He pointed out some of the contradictions in Way's paper, but at the same time he accepted the erroneous conclusion that the exchange is irreversible. Liebig's contempt for Way's experiments is shown by the following quotation: "Agriculture cannot be advanced by agricultural chemical experiments of this kind".

Later (1858), Liebig reported a few experiments on cation exchange, the results of which verified Way's data, but which shed no new light on the subject. He rejected the idea that the absorption of NH_4 or K is caused by a single substance and pointed out that many kinds of substances have this power. Liebig believed that the absorbed bases are held within the capillaries of the soil by a physical force similar to that by which water is held in a sponge. Owing to the commanding position of Liebig in the scientific world of his day, his disagreement with Way led to a controversy among soil scientists which raged for several decades. As Fisher (1922) pointed out, a great deal of time and energy was wasted in debate over the question: Is the exchange process chemical or physical?

Eichhorn (1858) found that upon treating chabazite, a naturally-occurring crystalline Ca-zeolite, with a solution of NaCl or NH_4Cl , Ca is replaced with the formation of soluble CaCl_2 . Na or NH_4 in the form of Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ also replaced Ca from chabazite, but in this case insoluble CaCO_3 was formed. On the other hand, when the Na-zeolite, natrolite, was treated with a solution of CaCl_2 , but little Na was replaced. From these experiments, Eichhorn concluded that the order of the replacing power of Ca and Na suggested by Way is incorrect. However, he found that the replacement of Ca from chabazite by Na or by NH_4 is reversible, the only difference between the two being in the rates of the reaction.

Henneberg and Stohmann (1858) confirmed Way's conclusion that the amount of NH_4 which can be absorbed by a given soil depends on the concentration of the solution and the ratio of solution to soil used. With equal concentrations and ratios, approximately the same amounts of NH_4 were absorbed from solutions of NH_4Cl , NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$, but somewhat greater amounts were absorbed from NH_4OH , and still greater amounts from $(\text{NH}_4)_2\text{HPO}_4$. When a solution containing equivalent amounts of both NH_4Cl and NH_4OH was used, more of the latter than of the former was taken up by the soil.

This last-named experiment led the authors to conclude, in agreement with Way, that two different kinds of reactions are involved, one with neutral salts and another with alkaline compounds. This confusion persisted for many years, and was only cleared up when it was found that the H ion is often involved in the exchange process. That greater amounts of NH_4 were taken up from $(\text{NH}_4)_2\text{HPO}_4$ than from NH_4Cl solution was explained only after it became known that Ca ions replaced by NH_4 ions are precipitated as an insoluble phosphate, which influences the equilibrium. Henneberg and Stohmann were the first to recognize that, to demonstrate the stoichiometry of cation exchange, it is necessary to distinguish between exchange and pure solubility, and that, in addition to water-soluble salts, CaCO_3 must also be considered, since CaCO_3 is distinctly soluble in many salt solutions.

Peters (1860) showed that natural soils may contain exchangeable Mg and Na ions in addition to Ca ions, and that the replacement of all these cations is influenced by concentration of the solution and ratio of solution to soil. He also reported that K ions, taken up by exchange, can be replaced by Na, Ca, or Mg ions, and most readily by NH_4 ions. On the other hand, Peters claimed that the power of Mg, NH_4 and Na ions to replace Ca ions from natural soil stand in the order: $\text{Mg} > \text{NH}_4 > \text{Na}$. Thus according to Peters, the relative replacing power of Mg and NH_4 ions depends on what kind of cation is being replaced, NH_4 being more effective than Mg in the replacement of K, while the reverse is true in the replacement of Ca. As will be shown later, the kind of substance with which the exchangeable cation is combined, also influences the exchange reaction.

Peters found that the rate of cation exchange is rapid, about two thirds as much K ions being taken up by exchange in $\frac{1}{4}$ hour as in

14 days. Exchangeable K ions are relatively insoluble in distilled water, but considerably more so in dilute acids. It is interesting to note that Peters found that the amounts of exchangeable K brought into solution by carbonic, acetic and hydrochloric acids increased with the ionization of these acids. Although it was not known at the time that H ions can replace metallic cations, Peters' results were undoubtedly due to exchange with H ions and not to pure solution processes, as he thought.

Peters also considered the question, is the exchange of cations a physical or a chemical process? Having found (1) that previous extraction of the soil with HCl largely destroyed its power to absorb K ions from neutral salts, (2) that treatment of the acid-extracted soil with CaCl_2 partially restored its power to absorb K ions, and (3) that treatment with CaCO_3 restored it completely, Peters concluded that the presence of some other metallic cation is a necessary condition for the absorption of K ions, and that the function of the cations is to neutralize insoluble acids. Peters' results are now explained on the basis of H-ion replacement.

Here we see again that the undeveloped state of knowledge caused the early investigators to draw erroneous conclusions. However, since the present understanding of cation exchange, although vastly more advanced than in 1860, is certainly still far from complete, some of the views now generally accepted will almost certainly have to be revised in the future. Hence, the soil scientist should avoid dogmatism. Present-day views may indeed undergo fully as great revision in the future as theories of the past.

Peters found also that the absorption of K by soils is not proportional to the humus content of the soil, but is roughly proportional to the content of fine-grained material. This he interpreted as evidence that the process is a manifestation of surface attraction, and therefore essentially physical.

Frank (1866) placed soil in a 3-inch brass tube that was provided with outlets at the bottom and also at various intervals along the sides of the tube. He first leached the soil with distilled water and then with a one per cent solution of KCl. He noted that the water remaining in the soil after leaching with water was displaced out ahead of the KCl solution. This was one of the first records of displacement, antedating by several decades the more systematic experiments on displacement. When the Cl content of the solution

which drained from the bottom of the tube became equal to that of the original KCl solution, samples were drawn off from several of the drainage outlets along the sides of the tube. The solution drawn out 12 inches below the surface of the soil was found to contain only 9 per cent of the original K content, that is, 91 per cent of the K had been taken up by the soil. The K content of the drainage progressively decreased with depth in the column; at a depth of 6 feet the solution contained only $2\frac{1}{2}$ per cent of the original K content. Since the drainage at any point in the column represented solution that had passed through the overlying soil, these results show that the total amount of K taken up by the soil depends on the amount of soil through which the solution passes.

Frank found that the addition of NaCl to the KCl solution reduced the absorption of K from that solution. He also noted that K, previously taken up by the soil, can be replaced by Na ions. This, of course, denotes that K and Na ions are mutually exchangeable.

Frank observed that acid soils impart an acid reaction to salt solutions, and Solomon (1867) suspected that soils in general have this effect on salt solutions. Accordingly, he provided for the neutralization of acids that are formed when neutral salts are added by adding NH_4OH to his salt solutions. With the use of an alkaline solution of $\text{Ca}(\text{NO}_3)_2$ different amounts of Ca were absorbed by different kinds of soil, and with certain soils the amount of Ca absorbed was roughly proportional to the concentration of the solution used, while with other soils this was not the case.

The fact that neutral salt solutions are made acidic by contact with soil was interpreted at this time not as evidence that H ions are replaced but that the process was purely physical, the idea being that the cation of the solution is absorbed, leaving the acidic part of the salt, the anion, in solution.

Biedermann (1869) found that soils differ widely in their power to absorb K and that temperature has but little effect on the process. He suggested that mica may be formed upon adding KCl, thus antedating Volk's (1934) conclusion by almost a half century that muscovite is formed upon adding a K salt to certain soils.

Heiden (1869) found that the amount of Mg absorbed from MgSO_4 solution was approximately equivalent to the sum of the Ca, K, and Na replaced. This led him to the conclusion that the

cation-exchange process is essentially chemical. He also concluded that both hydrous silicates and humus take part in the exchange process.

Knop (1872) (1874) correlated the NH_4 -absorbing power of soil with what he called "aufgeschlossenen Silicatbasen", that is, silicate bases soluble in 5 per cent HCl. Knop believed (1) that certain specific kinds of substances, namely, hydrous aluminum and iron silicates, are responsible for the absorption of NH_4 , (2) that the process is essentially chemical, (3) that the crop-producing power of the soil is not necessarily correlated with its NH_4 -absorptive power, and (4) that the NH_4 -absorptive power is roughly proportional to the amount of fine-grained material present, which was Way's conclusion also. That the power of absorbing NH_4 is not necessarily proportional to the amount of clay material present, is largely due to the fact, as will be shown later, that different kinds of clay differ greatly in their cation-exchange power.

Biedermann (1872) also sought to correlate the absorptive power with "aufgeschlossenen Silicatbasen". He found that this correlation was good with certain soil, but not with others. He added CaCO_3 before treating the sample with NH_4Cl on the theory that NH_4Cl is first split into NH_3 and HCl, and that some basic substance must be present with which HCl can combine. The cation released was thought to be due to the solvent power of the HCl rather than to replacement by NH_4 ions. This idea was held by other workers of this period.

It should be pointed out in this connection that the quantity, reported by Biedermann and others of this period as absorptive power, was not necessarily the same as that now called *cation-exchange capacity*, since equilibrium rather than leaching conditions were used.

Pillitz (1875) appears to have been one of the first to employ leaching conditions in the study of this problem. He used a series of concentrations of NH_4Cl and found that the maximum amount of NH_4 was absorbed from a 7.2 per cent solution (approximately 1.3 N). He found that soils differ in their power to absorb NH_4 , but that under constant temperature and pressure every soil has a maximum absorptive power. This is the first record of the now well-known fact that under a given set of conditions the cation-exchange capacity of every soil is a definite quantity.

Pillitz showed that under like conditions equivalent amounts of K and NH_4 ions are absorbed by a given soil. However, he drew the erroneous conclusion that, when a soil is once saturated with one base, it no longer has the power to absorb any other base. Apparently he looked upon absorption as the satisfying of the attractive forces of the soil, and, once these forces are satisfied, the soil no longer is able to absorb any base. This is analogous to the idea that the function of the added base is to neutralize soil acids. Although Pillitz' researches were published 25 years after Way's papers, it is probable that he was not familiar with Way's publications.

Lemberg (1876) showed in an important paper that crystalline silicates other than zeolites also exchange cations with salt solutions. By treatment with a Na salt solution, he was able to convert leucite, an anhydrous K mineral closely related to the feldspars, into analcite, a Na mineral, and then to reverse the process by treating analcite with KCl solution. Thus by cation exchange one crystalline silicate was converted into another. More recently Vanselow (1932a) verified Lemberg's results. This work of Lemberg is important in its bearing on the argument concerning the nature of the cation-exchange process.

Van Bemmelen (1878) (1879) published two papers under the title "Das Absorptionsvermögen der Ackererde". His conclusions were:

- (1) Zeolitic silicates, soluble in HCl, are responsible for cation exchange in soils. The exchangeable bases are chiefly Ca and Na with lesser amounts of Mg and still less K.
- (2) Absorption of hydroxides and salts of strong bases and weak acids by soils takes place without exchange. [Way's conclusion (5).]
- (3) The power of the soil to exchange cations with neutral salts is destroyed by boiling with strong HCl, but this power is restored by subsequent treatment with hydroxides or salts of weak acids, such as boric and carbonic acids.
- (4) The exchange process is a true chemical reaction.

As Gedroiz (1918, p. 275) pointed out, "Van Bemmelen fully joined those who believed in the chemical nature of exchange reactions in the soil; even more than that, none of the previous investigators expressed himself so definitely in favor of this theory".

Van Bemmelen (1879) claimed that KOH is absorbed by acid-treated soil, but not KHCO_3 . Therefore, since K_2CO_3 hydrolyzes to form KOH and KHCO_3 , the amount of K absorbed from salts of weak acids can never exceed $\frac{1}{2}$ of the K added. This conclusion is now known to be entirely erroneous.

The Colloidal Concept

Van Bemmelen's Hydrogels. In 1888 Van Bemmelen revised his views radically. As a result of studies on hydrogels, he abandoned the chemical explanation of cation exchange and also largely reversed himself in regard to the zeolitic hypothesis, substituting "absorption exchange" and "absorption compounds". His conclusions are best stated in a free translation of his own words:

"Absorption compounds are formed from components with variable molecular ratios. They should be distinguished from chemical compounds, but they may change into chemical compounds. Colloidal substances form such absorption compounds with water and other liquids, with bases, acids, and salts. . . . The absorptive power diminishes as absorption takes place. At equilibrium the relation between a colloid and a solution is a complex function of concentration and temperature. The absorbed substances may be exchanged for other substances of a solution, the bases being thereby exchanged in equivalent amounts. Colloids may often bring about chemical decomposition of salts as a result of their absorptive power.

"The soil contains colloidal silicates, iron oxide, silicic acid and organic substances; all these may bring about the above-mentioned results. The phenomenon of absorption observed upon treating a soil with a salt solution may be ascribed chiefly to colloidal silicates; its absorptive power for the whole salt is negligible".

Thus Van Bemmelen traces the absorptive (exchange) power of the soil to its content of hydrogels. Acids decompose these hydrogels and therefore destroy the absorptive power. According to Van Bemmelen the hydrogels are composed of indefinite proportions of $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, SiO_2 , and humus, any one of which can itself form a hydrogel and which has an absorptive power peculiar to itself. Hence, mixtures of these substances vary in absorptive power, depending on the relative amounts of each present. Therefore, soils which contain equal total amounts of colloidal material may vary considerably in absorptive power.

Although hydrogels were considered to be chiefly responsible for the absorptive power of the soil, Van Bemmelen concluded that soils may also contain small amounts of zeolites which take part in the absorptive (exchange) process. He pointed out that the reaction between the zeolites and salt solutions must be chemical, but that taking place with hydrogels is physical.

Thus Van Bemmelen made a distinction between reactions involving crystalline substances and those with colloidal substances. Van Bemmelen was not aware that crystalline substances may also be highly colloidal and that the so-called colloidal substances of soils are definitely crystalline. The work of Van Bemmelen was the forerunner of numerous papers on colloidal phenomena in relation to cation exchange.

For a period of about 20 years following the publication of Van Bemmelen's 1888 paper, no important paper on cation exchange was published.

Work of Wiegner. Van Bemmelen's paper, together with Way's publication, stimulated Wiegner to investigate cation exchange from the standpoint of colloid chemistry. In 1912 he concluded that permutite, prepared like Way's material, and also natural soils, contain adsorption compounds which are responsible for their cation-exchange power; that cation exchange is an adsorption reaction rather than a chemical reaction, and that the exchangeable cations are held on the surface of particles, and within capillaries, not by chemical attraction but by adsorption.

Later, Wiegner and his students published a large number of papers on cation exchange, practically all of which approach the subject from the standpoint of colloidal phenomena. The material used was chiefly permutite. In a general review of this work, Wiegner (1931a, 1931b) set forth his views on cation exchange quite fully and definitely.

According to Wiegner, cation exchange is an adsorption reaction and not an ordinary chemical reaction. Each particle of the exchange material, whether permutite or soil, is made up of three parts: (1) a kernel called "micron" or "ultramicon", (2) a layer of adsorbed anions external to the kernel but lying in contact with it, (3) exchangeable cations attracted to the particle by the adsorbed anions. These cations are supposed to form a sort of swarm around the particle and in an aqueous medium they are more or less hydrated. In some cases the adsorbed anions consist of OH ions

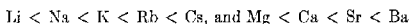
exclusively, in others of both OH and silicate ions. Diagrammatically Wiegner's concept of a H-saturated, three-component system, is shown in Figure 1.

Although Wiegner repeatedly emphasized that cation exchange is an adsorption reaction and not chemical, he stated, in explanation of the effect of the ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$, that a high ratio (3 or 4:1) is favorable to cation exchange, since "silicic acid, which exists on the inner coating of the ultramicros, can show greater exchange than aluminum hydroxide because the conditions for the dissociation of silicic acid are more favorable than for aluminum hydroxide". Here Wiegner practically suggests that cation exchange is an ordinary chemical reaction.



FIGURE 1. Wiegner's concept of the ion swarm

Wiegner arranged the cations in the order of their replacing power as follows:



which is the Hofmeister lyotropic series. However, as will be discussed later, the relative replacing power of the cations depends on at least two variables, namely, (1) the kind of cation being replaced, and (2) the kind of exchange material. This indicates that there is but little significance to any one order of replacing power.

Wiegner also emphasized ion size and ion hydration as factors in exchange. As is well known, different cations become hydrated to different degrees and hydration presumably increases the effective size of an ion. As a general rule, Wiegner concluded that the smaller the ion the greater its replacing power. The idea that

hydration tends to reduce the replacing power of an ion is confirmed by the results of Wiegner and Jenny (1927). They found that the replacing power of Na ions is increased by adding alcohol to the solution. Whereas in an aqueous solution Na ions replaced 0.64 m.e. of Ca ions from Ca-permutite, in 80 per cent alcohol the same concentration of Na ions replaced 1.23 m.e. of Ca ions. Further, although Cs ions were substantially more effective than Na ions in water, they were approximately equal in replacing power in 80 per cent alcohol. Presumably the ions—both the solution and exchangeable forms—were much less hydrated in the alcoholic solution than in water.

As will be shown later, the importance of ion size in exchange reaction is by no means certain. Obviously, any ion, whatever its size, must be able to gain access to the so-called "exchange spots", that is, the electric field in which the adsorbed ion is held by the solid particle.

Wiegner's explanation of the low cation-exchange capacity of kaolinite is interesting: "We consider this to be explained by the fact that, with increasing aluminum content, the part played by hydroxyl ions in the inner swarm of ions increases, and thereby the adhesion of the outer exchange ions also increases". The untenability of this explanation, as well as that of the three-compartment system (ultramicros, inner layer of adsorbed anions, and outer swarm of cations) will be shown in Chapter 2.

Gedroiz' Researches. The most comprehensive series of investigations on cation exchange was that published by Gedroiz (1912, 1914, 1916, 1918, 1919, 1922, 1924a, 1924b, 1925). These papers discuss many important aspects of cation exchange, such as: (1) The influence of each of several exchangeable cations on the chemical, physical and plant nutritional properties of the soil. (2) The speed of the exchange reaction and the replacing power of different cations. (3) Methods for the determination of exchangeable cations. (4) Cation-exchange capacity of soils. (5) The relation of exchangeable Na to alkali and saline soils and to the formation of Na_2CO_3 in soils. (6) Exchangeable cations in relation to chernozems and podzols. (7) Base unsaturation and the degradation of soils. (8) The nature of the exchange material. Special phases of this work will be discussed in subsequent chapters.

Gedroiz (1922) held that cation exchange arises from the fact that

the exchange material is colloidal and that the exchange reaction is an aspect of colloid chemistry. Colloid chemical reactions are contrasted with ordinary chemical reactions. He says (p. 38): "Actually it is impossible to explain the exchange of bases between the soil and solution from a purely chemical point of view". Rather the reaction is considered to be a physicochemical reaction.

According to Gedroiz (p. 39), the energy of the reaction arises from surface tension. "There is here a so-called energy of absorption, due to the existence of the force of surface tension at the limit of contact of solid and liquid phase. This energy is proportional to the amount of surface tension and the amount of surface of the solid phase". He states further (p. 40): "If the solid phase is sufficiently finely divided, it is not necessary at all for it to go into solution in order for the reaction with a substance in solution to take place energetically. But such reactions can take place only on the surface of the solid", either an external surface or an accessible internal surface. "We must look, therefore, upon the exchange of soil zeolitic cations for the cations in solution in contact with the soil, as upon a purely physical process, taking place only on the surface of solid particles, and its source of energy is the surface energy of the system".

Throughout his papers, Gedroiz referred to the inorganic exchange material as zeolitic material, but not zeolitic in the mineralogical sense. He states (p. 17): "We now know definitely that soils do not contain any mineral zeolites, but we preserve the historical name, giving it another meaning, namely, *under the zeolitic part of the soil we signify that aluminosilicate complex which is capable of exchanging its bases for the base of a salt solution*. Those cations which are found in humates and which are capable of exchanging for NH_4 ions are called humic cations".

Mattson's View. Beginning in 1929 and continuing to the present time (1947), Mattson has published a series of papers in *Soil Science* under the general title: "Laws of Soil Colloidal Behavior", in which cation exchange is explained on the basis of acidoid-basoid ratio. Within certain limits, the exchange capacity of permutite-like precipitates has been found to increase somewhat parallel to the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio, and the same is true in a general way with soil colloids. Mattson's (1930) explanation of this relationship differs from Wiegner's hypothesis and from all others previously proposed. He holds that in these precipitates silicic

acid (acidoid) may be combined with $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ (basoid) in a variety of ways, depending largely on the relative amounts present and the pH of the medium. This determines what the exchange capacity will be.

At the isoelectric point, whatever it may be for a particular sample, equivalent numbers of cations and anions dissociate; on the acid side of the isoelectric point, the dissociation of anions (chiefly OH ions) exceeds that of cations. In this pH range, anion exchange is active and may equal or exceed that of cation exchange. Above the isoelectric point, cation dissociation predominates. Mattson explains cation exchange on the basis of ionization. His explanation, unlike Wiegner's hypothesis, does not presuppose the adsorption of OH or SiO_3 ions. The three-component system of Wiegner is replaced by a two-component system, namely, the solid particle surrounded by dissociated cations. The latter are represented as a swarm of cations, as in Wiegner's scheme. When a salt solution is added, Donnan distribution is assumed to take place, and cation exchange is merely the consequence of the Donnan distribution principle.

Mattson has discussed various aspects of colloidal behavior, its relation to cation exchange, Donnan effects, coagulation, soil formation, etc. One point emphasized by Mattson (1932) should be mentioned here, namely, cation-exchange capacity is a function of pH. At a given pH the exchange capacity is a definite quantity for a given sample, but different from that at another pH. Therefore, whenever cation-exchange capacity is stated, the pH should also be given; otherwise the term "exchange capacity" has no definite meaning. This is an important point to which further reference will be made later.

In the course of Mattson's researches, extending over a period of about 20 years, his ideas have undergone some change. As new evidences were obtained, previous explanations have been modified. The result is apparent contradiction in statements. This, however, should be looked upon as evidence of the evolution of his ideas, and cannot be rightly criticized.

The Clay Mineral Concept

The discovery by Hendricks and Fry (1930) and by Kelley, Dore and Brown (1931) that the inorganic colloidal material of the soil is commonly crystalline, ushered in a new period in soil science.

From this discovery a wholly new concept of cation exchange has been developed. Instead of being due to hydrogels (Van Bemmelen), to the adsorption of OH and SiO_3 ions (Wiegner), to zeolite-like material (Gedroiz and others) or to acidoid-basoid ratio (Mattson), cation exchange in soils is now known to be occasioned by the crystal structure and lattice composition of the clay minerals.

In the formation of the more important cation-exchange clays, the arrangement of the electronegative O and OH ions and the electropositive Si, Al, Fe, and Mg ions is such as to necessitate the taking up, from the medium, cations in addition to those in the structural framework of the crystal lattice. These cations are located on the exterior of lattice layers and are held by electrostatic attraction. They tend to dissociate and in consequence they are replaceable by other cations in solution. This is now the prevailing view among soil scientists and mineralogists. It is supported by strong experimental evidence. The researches on clay minerals have placed cation exchange on a rational basis. A full exposition of the clay mineral concept will be given in Chapter 2.

Period of Application

About 1910 soil scientists began to explore the phenomena of cation exchange on a wide scale. Along with the development of quantitative methods, the exchangeable cations have been determined in soils from all parts of the world. For some time this determination has become routine in soil laboratories generally. It has been found that the exchangeable cations are intimately connected with many different soil processes. These cations are involved in reactions with fertilizers, in soil physics, soil chemistry, soil acidity, the buffer properties of the soil, and in alkali soils. These phases of cation exchange will be more fully discussed in the following chapters.

Chapter 2

The Cation-Exchange Material

As was pointed out in the preceding chapter, Way found that cation exchange is a property of the clay material of soils, and that the active substance is a hydrated aluminosilicate. Following the publication of Way's experiments, many soil scientists have sought to determine the specific nature of the substances involved. The determination of this question is fundamental to an understanding of cation exchange, for, as is well established in chemistry, knowledge concerning the specific nature of a substance is essential to an understanding of the properties of that substance. It seems desirable to trace the development and evolution of ideas about the cation-exchange material of soils.

ORGANIC SUBSTANCES

A few years after Way's papers were published, Rautenberg (1862) concluded that soil humus plays a significant part in cation exchange. Heiden (1869) and others of this period came to the same conclusion. More recently it has become certain that a considerable part of the cation exchange of soils in general is due to organic substances. However, this monograph is devoted primarily to the inorganic materials and therefore only brief reference will be made to organic substances. This does not mean that organic substances are unimportant. As a matter of fact, quite the contrary is the case. But despite many publications, our knowledge on the organic material is not well advanced. A comprehensive review of the literature on the organic material is given by Gehring (1931).

There appears to be an intimate connection between organic and inorganic exchange material in soils; but the nature of the connection is far from clear. Preparatory to the study of the inorganic material, it is common to remove the organic substances by oxidation with H_2O_2 , and to consider the accompanying loss in exchange capacity as having been caused by this removal. It is by no means certain that this assumption is justified. If justified, it means that

the contribution of the two kinds of material is purely additive. It seems probable that the exchange property of the one is affected to some degree at least by intimate combination with the other.

Humic Acids

For many years soil scientists held that the part played by organic matter in cation exchange was traceable to the so-called humic acids. The exact nature of these substances is unknown. However, it is well established that soil humus, when largely freed from metallic cations, exhibits acid properties. Upon adding neutral salt solutions to this material, acid solutions are obtained through exchange for H ions. Acid humus is practically insoluble in water. When treated with a Ca salt, an insoluble substance containing replaceable Ca ions is obtained; whereas the corresponding K, Na and NH_4 compounds are more soluble and more highly dispersed.

By suitable means humus-like material can be prepared from various pure substances, such as sucrose, starch, etc., but this material is different in several respects from the natural humus of ordinary soils. Among other things, natural humus always contains nitrogen, but, as Waksman (1938) pointed out, the material is probably never composed of a single chemical compound. Generally it appears to be a complex mixture of substances, variable, depending partly on the kinds of plant and animal materials from which the humus has been formed, and partly on the conditions under which these materials have undergone decomposition. The prevailing view of soil microbiologists is that soil humus represents the relatively resistant organic residue remaining from the action of microorganisms on dead vegetable and animal materials, together with certain products of microbiologic origin.

Since the humus of soils in different localities is variable, it is not surprising that the cation-exchange capacity of humus is also variable. For this reason, it is not possible to calculate general combining weights of humus (see Hissink, 1924), any more than it is possible to calculate a general exchange capacity of soil clay. The values must necessarily vary from soil to soil.

Ligno-Proteins

From researches on humus, DuToit and Page (1930, 1932) came to the conclusion that lignin, or some related substance, is a con-

stituent of humus. According to Waksman (1938), soil humus is a mixture of substances consisting of variable ratios of more or less altered cellulose, hemicellulose and lignin combined with proteins of microbiologic origin. He produced a substance experimentally by combining lignin with protein which had properties similar to those of soil humus.

The exact nature of the combination between lignin and protein in the artificial product is not known. The material was found to be quite stable and relatively resistant to decomposition by micro-organisms. The cation-exchange property of so-called ligno-protein is thought to be caused by the acid ionization of residual COOH groups. It is possible that sulfonic and phenolic groups are also involved.

It is by no means certain that the precipitated ligno-protein of Waksman is similar to the active substance in soils. If the soil substance has been derived in part from lignin, the latter must have undergone deep-seated changes, as is indicated by recent investigations of Gottlieb and Hendricks (1945).

INORGANIC MATERIAL

Zeolites

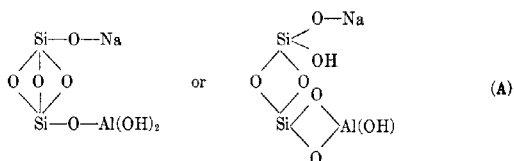
Eichhorn (1858) showed that the Ca of chabazite, a crystalline Ca-aluminosilicate, can be replaced by K ions by leaching with a solution of KCl, and that the reaction is reversible. This work, together with Way's investigations on artificial aluminosilicates, lead quite naturally to the view that the cation-exchange material of soils is of a zeolitic nature. Stremme (1910) concluded that soils contain amorphous zeolitic material which is essentially like natural crystalline zeolites. He even referred to halloysite and montmorillonite as being similar to allophane rather than being crystalline, as we now know these minerals to be. As late as 1928 Kerr referred to the soil material as zeolitic. He proposed the formula $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ for the artificial material, and he seemed to infer that this formula applies to the material of natural soils.

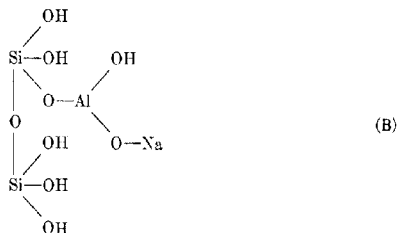
Numerous other investigators have drawn similar conclusions. Such expressions as "soil zeolites", and "zeolitic cation-exchange material" are in common use in soil literature of the present day. However, no convincing evidence in support of the zeolite hypothesis has been presented. In fact, there is strong evidence against the

occurrence of true zeolites in soils. Kelley, Dore, and Brown (1931) pointed out that the clay material, which, as Way first suggested, is the seat of the greater part of the cation exchange of mineral soils, is the most highly weathered, and, with the exception of quartz and a few other minerals, the most stable part of the soil. Zeolites, on the other hand, are relatively unstable. Granting that zeolitic material may be formed in the early stages of the weathering of igneous silicates, such compounds could hardly persist in soils because of their instability under more drastic weathering conditions. They would almost certainly be decomposed before the weathering reached an advanced stage. The cation-exchange material is fairly stable in dilute acids. Jacob *et al.* (1935) found that the cation-exchange capacity of certain soil colloids was not greatly reduced by digestion with concentrated HCl. On the other hand, crystalline zeolites are readily decomposed by acids. It is true that a part, at least, of the exchangeable cations of zeolites can be replaced by H ions, but this is usually accompanied by more or less decomposition of the sample.

Permutites

Way's experiments with artificial aluminosilicates initiated the use in exchange experiments of the material called permutite. Ganssen (1908) and many others have conducted numerous experiments with permutite prepared in different ways. Permutite is widely used in the softening of water for domestic and industrial uses. In this process Ca and Mg ions are removed from the water by exchange with Na ions of the permutite. Ganssen noted that the cation-exchange power of permutite depends on the method of preparation. The product formed by precipitating $AlCl_3$ with Na-silicate is much less active than the product obtained by precipitating Na-aluminate with Na-silicate. The former was called aluminum double silicate, the latter aluminate silicate. Ganssen pictured these substances as follows:





Thus Na ions in the aluminosilicate (A) are supposed to be attached through O ions to Si ions, in which case Na is not readily replaceable. When attached through O to Al ions, as in the aluminate silicate (B), the Na ions are said to be readily exchangeable. These formulas are purely hypothetical. Although Wiegner and others have made extensive use of permutites in cation-exchange investigations, this kind of substance does not occur in ordinary soils. As will be shown later in this chapter, the soil material is neither permutite-like nor zeolitic.

Colloidal Nature of the Exchange Material

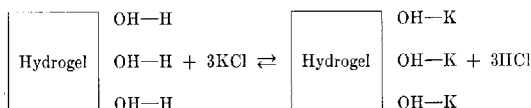
Hydrogels. The idea that the exchange material is colloidal originated from the work of Van Bemmelen (1888). In his paper he discussed hydrogels, such as are formed under certain conditions by $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ or SiO_2 . He advanced the idea that when in contact with a salt solution, the gels absorb the salt, and that the water solution within the gel may even become more concentrated than the outside solution. The absorbed salt tends, according to Van Bemmelen, to combine with the gel substance, forming "absorptions Verbindungen" of indefinite composition, the cations of which are exchangeable.

Gedroiz' Idea. The inorganic-exchange material of soils, according to Gedroiz (1922), is either (a) extremely fine-grained rock fragments, or, (b) mutually precipitated colloidal silicic acid, $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. Regarding the origin and mode of formation, he suggests two possibilities: (1) During the course of weathering, rocks and minerals are broken down into finer- and finer-sized particles culminating in particles of colloidal size. The absorptive power of the particles simultaneously increases, reaching a maximum in the colloidal range owing to the high specific surface. Cat-

ions, absorbed from the natural solutions that come into contact with the particles, are exchangeable; (2) the exchange material may be looked upon as a new formation which was not present in the original rocks. "It is quite possible that, under certain conditions, the colloidal hydroxides of silicon, aluminum and iron, formed in the weathering of rocks and soils, mutually precipitate, since at least colloidal silicic acid usually carries an electric charge opposite to that of aluminum and iron hydroxides. The precipitated mixed gels of these compounds carry with them various substances from solution, and among others, the cations present".

Gedroiz pointed out that it is quite possible that a substance so formed occurs in soils, "but we have no direct data in regard to its actual existence in soils". He suggested, however, that both types of material and methods of formation are probably involved in soils.

Adsorption of OH Ions. Wiegner (1912) noted that many kinds of colloidal particles migrate towards the positive pole in an electric field. Hence they are said to be electronegative. He explained this by assuming that the particles adsorb OH ions, thereby acquiring a negative charge. The particles first attract OH ions and in consequence they then attract cations, and these latter are said to be exchangeable. For example:



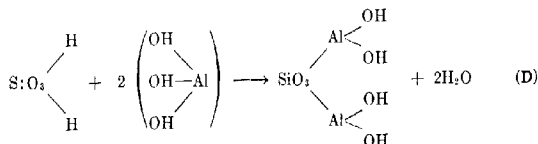
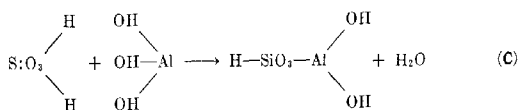
Later Wiegner (1925) pictured the exchange particle as being composed of three parts, (1) a kernel, (2) a layer of adsorbed anions lying close to the kernel and consisting of OH or SiO_3 ions, and (3) a diffuse swarm of exchangeable cations surrounding the particle and attracted to it by the adsorbed anions.

Thus Wiegner explained the electronegativity and the cation-exchange power of soil colloids on the basis of the adsorption of OH ions or SiO_3 ions.

Wiegner (1931a) attempted to reconcile the cation-exchange property of crystalline zeolites with colloidal properties by saying that zeolites undergo "internal dispersion". As used by Wiegner, internal dispersion refers simply to dissociation of cations in the cavities and channels within the crystals.

Isoelectric Precipitates. Mattson (1931a, 1931b) concluded that the inorganic exchange material of soils is of the nature of isoelectric precipitates. These, in large part, are composed of $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ called (basoids) combined in various proportions and in different ways with silicic acids (acidoids). The mode of combination depends on the proportions of basoid and acidoid and more particularly on the pH of the medium. The isoelectric pH depends on the ratio of basoid to acidoid, and in turn the precipitate formed will tend to have that percentage composition which is most nearly isoelectric at the prevailing pH.

According to Mattson and Hester (1932), isoelectric precipitates are not mere mechanical mixtures, but chemical compounds, the chemical combination being effected by the union of one or more of the acidoid H ions and basoid OH ions with the splitting off of H_2O . The remaining H ions of the silicic acid are thought to be the seats of cation exchange. At pH values above the isoelectric point, the residual OH ions of the basoid tend to ionize as acids. Therefore, at high pH the cation-exchange capacity may be largely determined by the residual OH ions. Extreme types may be illustrated as follows:



According to Mattson, compounds like (C) will have strong cation-exchange power, owing to the dissociation of the residual H ions of the acidoid, while compounds like (D) will have practically no cation-exchange power at or below the isoelectric point, but at high pH the residual OH ions of the basoid will ionize as acids, and then the cation-exchange capacity will be pronounced, and may even exceed that of compound (C) at its isoelectric point.

Mattson holds that isoelectric precipitates are amorphous when

first formed, but on standing they tend to age, that is to crystallize, and in consequence the cation-exchange power is reduced. Whatever cation-exchange power the crystallized form possesses is due, according to Mattson, either to amorphous material adsorbed on the surface of the crystals, or to exposed cation on the surface of the crystals. The interior of the crystals was referred to by Mattson (1937) as "frozen matter" and plays no part in cation exchange.

The hydrogel, adsorption of OH ions and the isoelectric precipitate hypotheses and also Gedroiz' idea, are all based on the idea that the exchange material is amorphous and colloidal. However, Eichhorn, as early as 1858, showed that chabazite, a crystalline hydrous Ca-aluminosilicate, has cation-exchange property. Lemberg (1876) demonstrated that relatively coarse particles of leucite, $KAlSi_3O_8$, a mineral closely related to the feldspars, can be converted into analcite, $NaAlSi_3O_8 \cdot H_2O$, and vice versa by cation exchange. Sullivan (1907) showed that many other minerals are subject to cation exchange.

Indeed, it cannot be said that cation exchange is an essential property of matter in the colloidal state. Substances such as finely divided sulfur, gold, platinum and certain sulfides are classical examples of colloidal substances. Yet none of these substances show cation exchange to more than a very limited extent. In comparison with certain clays, their cation-exchange power is negligible.

When examined more closely, it becomes apparent that cation exchange is a property not peculiar to the colloidal state, as such, but to certain kinds of surfaces. Surfaces showing this property may or may not be ultramicroscopic or microscopic in dimensions, in fact particle size, as such, is no indication of cation-exchange property. Rather it depends on the nature of the exposed surface. In recent years colloid chemists have treated cation exchange as a phase of surface chemistry.

The Clay Mineral Concept of Cation Exchange

Hendricks and Fry (1930) and Kelley, Dore and Brown (1931) discovered that the fine-grained inorganic material of soils is crystalline. This discovery soon led to the identification of the specific substances that are responsible for cation exchange in soils. These substances are chiefly the clay minerals, montmorillonite or beidel-

lite, hydrous mica, kaolinite and halloysite. This discovery has placed cation exchange on a more rational basis than was previously possible.

Pauling (1930) and other mineralogists have established the information that is basic to an understanding of the clay minerals. Hofmann, *et al.* (1933), Marshall (1935), Ross and Hendricks (1941, 1945), and others have extended this knowledge particularly in regard to the crystal structure of clay in relation to cation exchange.

Crystal structure and isomorphism, as understood by mineralogists, are the keys to an understanding of the cation-exchange material. For this reason a brief discussion will be given on crystal structure and isomorphism.

It is well established that the clay minerals are platy, resembling in this respect pyrophyllite, the micas and talc. They are characterized by a layer lattice structure. The layers are composed of planes of Si ions in which each Si ion is situated at the center of a tetrahedron formed by four O ions, and planes of Al, Fe or Mg ions surrounded by six O or OH ions arranged in the form of an octahedron. In kaolinite the lattice layer consists of one plane of Si tetrahedra bound to one plane of Al octahedra. In contrast, montmorillonite, beidellite and hydrous mica-type clays, the most important cation-exchange clays, contain lattice layers composed of two tetrahedral planes bound together by one octahedral plane. With montmorillonite, Si ions occupy the vast majority of the tetrahedral positions, possibly all of them, and the octahedral positions may be occupied by Al, Fe or Mg ions and some of them may be vacant. A substantial percentage of the tetrahedral positions of beidellite are supposed to be occupied by Al ions.

It is with reference to the octahedral plane of atoms that isomorphism is especially important in the montmorillonitic clays. Isomorphism implies the proxying of one ion for another in crystals. Whereas, Al ions comprise the only octahedral cations in pure pyrophyllite, some of these positions in montmorillonite may be occupied by Fe ions, and apparently Mg or Li ions are always present in octahedral positions. In order to make clear the significance of isomorphisms in relation to cation exchange, a brief description of certain closely related minerals will be given.

Pyrophyllite. Pyrophyllite is hydrous aluminum silicate of

the composition $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. The sequence of atomic planes in a lattice layer is:

		<i>Charges</i>	
Si—tetrahedra	6 O^{-2}	-12	
	4 Si^{+4}	+16	
Al—octahedra	4 O^{-2} , 2 $(\text{OH})^{-1}$	-10	-44
	4 Al^{+3}	+12	
	4 O^{-2} , 2 $(\text{OH})^{-1}$	-10	
Si—tetrahedra	4 Si^{+4}	+16	+44
	6 O^{-2}	-12	

The sum of the negative charges of O^{-2} and $(\text{OH})^{-1}$, (-44), just equals the sum of the positive charges of Si^{+4} and Al^{+3} , (+44). Therefore the pyrophyllite lattice is electrically neutral. When pure, pyrophyllite contains only traces of Ca, Mg, K or Na. Being electrically neutral the lattice is unable to attract ions save by weak van der Waals forces. Therefore it contains very little cation-exchange power.

Muscovite. Muscovite has the composition of $\text{K Al}_2\text{Al Si}_3\text{O}_{10}(\text{OH}, \text{F})_2$. It is also a layer lattice mineral, the atomic planes being:

		<i>Charges</i>	
Interlayer K^{+1}		+1	
Si—tetrahedra	6 O^{-2}	-12	
	3 Si^{+4} , 1 Al^{+3}	+15	
Al—octahedra	4 O^{-2} , 2 $(\text{OH}, \text{F})^{-1}$	-10	-44
	4 Al^{+3}	+12	
	4 O^{-2} , 2 $(\text{OH}, \text{F})^{-1}$	-10	
Si—tetrahedra	3 Si^{+4} , 1 Al^{+3}	+15	+42
	6 O^{-2}	-12	
Interlayer K^{+1}		+1	

Here we find that the charges of the ions comprising the framework of the lattice, that is the tetrahedra and octahedra, are out of balance by -2 charges, but this excess of negative charge is neutralized by interlayer K ions. According to Pauling (1930), the interlayer K ions share their charges between adjacent layers, thus binding them together. The bond is strong enough to prevent the entry

of water molecules between lattice layers. Therefore the crystal does not expand in water.

Neither pyrophyllite nor muscovite has pronounced cation-exchange power. This, in the case of pyrophyllite, is because the lattice layers are themselves electrically neutral. With muscovite, although the lattice framework is not neutral, the balancing K ions, as pointed out above, effectively hold the layers together and thus prevent these ions from entering into exchange with ions of solutions.

The balancing cations are essential to the integrity of the crystal; in fact they are parts of the crystal. According to Pauling's (1940) principle of microneutrality, the balancing cations must be as near the origin of the excess negative charge as possible. The principle of microneutrality undoubtedly applies to the clay minerals also.

Montmorillonite. X-ray evidence shows that, structurally, montmorillonite is similar to pyrophyllite and muscovite. It differs from these minerals, however, in these important particulars. (1) The (00l) spacings of montmorillonite are a function of the water content of the sample. This has been interpreted as meaning that water is able to pass in between lattice layers, causing the crystal to expand like an accordion. (2) Montmorillonite has pronounced cation-exchange power. (3) The crystals of montmorillonite are extremely small thin plates and usually irregular in outline.

The structural similarity between montmorillonite and muscovite, as shown by Hofmann, Endell and Wilm (1933), suggested to Marshall (1935) that isomorphous substitution would account for variations in chemical composition and the cation-exchange property of montmorillonite. Accordingly, he proposed a method by which the distribution of ions in lattice positions can be calculated from the chemical analysis. It is now widely accepted that the principle of isomorphism applies to the montmorillonitic clays.

While fully accepting the idea of isomorphism, Kelley (1945) showed that there are logical reasons why implicit confidence cannot be placed in the details of calculated formulas for montmorillonite. These reasons can be condensed into a simple sentence; namely, it is not possible to determine with certainty that the sample as analyzed was mineralogically pure. Amounts of various kinds of impurities, not detectable by any known method, might, if present, affect the results of calculation significantly.

Ross and Hendricks (1945) hold that small amounts of impurities do not invalidate the calculated formula for montmorillonite or other related minerals. On the basis of calculation they proposed formulas for montmorillonite and several other related minerals. The proposed formula for montmorillonite is $\text{Na}_{0.33} \text{Al}_{1.67} \text{Mg}_{0.33} \text{Si}_4 \text{O}_{10} (\text{OH})_2$. This was intended as a *hypothetical end member* formula, it being understood that more or less Fe^{+3} , Fe^{+2} , and minor amounts of several other elements may proxy for Al^{+3} in octahedral coordination and that limited amounts of Al^{+3} may proxy for Si^{+4} in tetrahedral positions. It was also concluded that the total cations in octahedral coordination may vary from 2, as provided for in the

Table 1. Montmorillonite, from Bentonite of Different Sources

Source	Water Loss on Ignition (%)	Cation-Exchange Capacity*	
		(m.e./100 gm) On Air-Dry Basis	On Basis of 4.91% H_2O
Death Valley, California	20.00	106	125
Otay, California	23.19	108	132
Clay Spur, Wyoming	19.61	89	104
Merritt, British Columbia	13.02	67	73
Rosedale, Alberta	12.56	90	97
Princeton, British Columbia	11.99	54	58
Goldfield, Nevada	22.72	101	123
Owyee, Wyoming	10.78	89	95
Newbery, California	22.79	115	140
Los Angeles, California (Master Products Co.)	21.10	90	107

* Determined by the neutral N ammonium acetate method.

formula, to about 2.2 per 12 O. The idea of isomorphism as applied to montmorillonitic clay was strongly supported by Ross and Hendricks and it is generally accepted by clay mineralogists. However, it is important to emphasize that the above formula does not represent any particular sample of montmorillonite, neither can it be said to be roughly representative of the average sample of montmorillonite, as will be shown in the following paragraphs.

Expressed on the air-dry basis, the cation-exchange capacity of montmorillonite from different sources has been found by experiment to range from about 60 to 115 m.e./100 gm (see Table 1), with many samples ranging from 90 to 105 m.e./100 gm. On the other hand, the exchange capacity, calculated from the proposed formula is 89.9 m.e./100 gm, but the OH ions of this formula cor-

respond to only 4.91 per cent H_2O , whereas, the air-dry form commonly contains from about 18 to 23 per cent total H_2O . Expressing the exchange capacity of material of the composition represented by the proposed formula on the basis of 21 per cent total water, which is close to the average H_2O content of many published analyses as well as many unpublished data, the capacity would be 77.4 m.e./100 gm. This is considerably less than that found for a majority of the samples that have been investigated.

A sample, having an exchange capacity of 60 m.e./100 gm expressed on the air-dry basis, would correspond roughly to the formula: $\text{Na}_{0.25}\text{Al}_{1.75}\text{Mg}_{0.25}\text{Si}_4\text{O}_{10}(\text{OH})_2$; while a capacity approximating 116 m.e./100 gm would correspond to the formula $\text{Na}_{0.50}\text{Al}_{1.50}\text{Mg}_{0.50}\text{Si}_4\text{O}_{10}(\text{OH})_2$.

Whether or not the presence of impurities is an obstacle to the calculation of a formula, variation in exchange capacity is an established fact, and this fact cannot be ignored in the calculation of a formula. These variations are so great that no single formula can possibly correctly express the composition of all montmorillonites. To accept any one formula for all samples would necessitate abandonment or substantial modification of the idea that the exchangeable cations are attracted to the lattice by the negative charges arising from the lack of balance between the electronegative and electropositive components of the structure, and there does not appear to be any valid reason for abandonment of this idea.

It is quite possible to correlate cation-exchange capacity with lattice composition and to show that the exchangeable cations are attracted to the lattice by its excess of negative charges, but this excess cannot be expressed by any single formula. Ross and Hendricks' hypothetical end member formula denotes that this excess is 0.33 per 12 oxygen atoms. However, there seems to be no reason why this particular quantity should characterize montmorillonite from all sources. In fact, there is evidence that variation in lattice composition is a feature of the montmorillonite from different parts of a single deposit of bentonite. The isomorphism of montmorillonite appears to represent a complex pattern. Among the specimens investigated, the excess negative charge varies at least twofold, but it probably never equals much more than half that of muscovite which is one charge per 12 oxygen atoms.

However, Ross and Hendricks' formula can be used, perhaps as

well as any other, to illustrate the relationship between montmorillonite and other structurally related minerals. This formula multiplied by 3 becomes $\text{Na Al}_3 \text{Mg Si}_{12} \text{O}_{30} (\text{OH})_6$, which corresponds to $1\frac{1}{2}$ crystallographic units, as revealed by x-ray analysis. The sequence of atomic planes is then:

		Charges	
Si—tetrahedra	9 O^{-2}	-18	}
	6 Si^{+4}	+24	
Al, Mg—octahedra	6 O^{-2} , 3 $(\text{OH})^{-1}$	-15	}
	5 Al^{+3} , 1 Mg^{+2}	+17	
	6 O^{-2} , 3 $(\text{OH})^{-1}$	-15	
Si—tetrahedra	6 Si^{+4}	+24	}
	9 O^{-2}	-18	
Interlayer Na^{+1}		+1	

As shown, the lack of balance on the lattice framework is compensated for by Na ions, or equivalent amounts of some other cation located on the surface of the lattice layer, just as the interlayer K ions balance the charges of the mica lattice. But, as stated above, this lack of charge balance within the layer is considerably less, quantitatively, than in the micas. In contrast to muscovite with approximately one excess negative charge per 12 oxygen atoms, this excess in montmorillonite may vary from approximately 0.25 to as much as about 0.50 per 12 O.

On the assumption that the excess negative charge is 0.33 per 12 O, Ross and Hendricks calculated a large number of samples drawn from many sources. With but one exception, the results showed a limited amount of Al in tetrahedral coordination. With many samples the amount of tetrahedral Al was less than one ion per 5 unit cells. It is highly probable that the cation-exchange property of this mineral is due quite largely to negative charges occasioned by deficiency of positive charges in the octahedral layer of the lattice.

Beidellite. It is well established that the mineral called beidellite is closely related to montmorillonite. According to Ross and Hendricks, there are a continuous series of isomorphous substitutions of Al^{+3} for Si^{+4} in the montmorillonite-beidellite series, ranging from practically no tetrahedral Al to as much as 0.82 Al^{+3} per 12 O. The calculations were made on the assumption that the

negative charge on the lattice was 0.33 per 12 O in each sample, and on other assumptions the correctness or incorrectness of which might influence the results substantially. The name beidellite has been applied by Marshall (1935) and by Ross and Hendricks (1945) to the more aluminous members of the series. In their discussion on soil clay, Ross and Hendricks (1945, p. 61) state: "Beidellite with a high content of ferric iron is probably the predominant soil clay mineral of the montmorillonite group". Nevertheless, they repeatedly designated soil clay simply as montmorillonite.

Ross and Hendricks also state: "As the beidellite end of the montmorillonite-beidellite series is approached there is a decided tendency towards the formation of mixed-layer-type minerals containing potassium. In more fundamental terms the number of non-exchangeable interlayer ions, essentially of K^+ , increases with the increase in replacement of silicon by aluminum in tetrahedral coordination. This indicates that there may be a complete gradation between the beidellite-type clay minerals and moderately high potassium mica-like minerals".

In contrast to the interpretation of Ross and Hendricks, the conclusion of Grim and Rowland (1942), based on thermal evidence, was that certain samples of alleged beidellite, including one from the type locality (Beidell, Colorado), are mixtures of montmorillonite and other hydrous minerals. Pask and Davies (1945, p. 69) suggest "that the name beidellite be retained for a series of minerals formed by the intergrowth or interstratification of kaolinite and montmorillonite instead of by isomorphous substitution of Al^{+++} for Si^{++++} in the silica sheets of the montmorillonite structure".

The conclusion of Ross and Hendricks that beidellite contains substantial amounts of tetrahedral Al^{+++} rests primarily on the results of calculation on the basis of chemical analysis, but the results of chemical analysis will certainly be influenced by interstratification of the sample. If the sample is actually interstratified, it is not possible to determine by calculation whether or not tetrahedral Al^{+++} is present in all the silica sheets of the sample or only in a part of them, or in none at all, as was made clear by the analysis of this problem by Kelley (1945). It is well known that the colloidal material of soils is rarely, if ever, mineralogically homogeneous.

The analyses of soil colloids from various localities show approximately as much Mg as is found in montmorillonite from many ben-

tonites, but this is not true of the 0.3μ colloid of certain Iowa soils reported by Russell and Haddock (1940). Assuming that all the Mg of these Iowa soil colloids was present in octahedral coordination, the amount found (0.38 to 1.10% MgO) was insufficient to account for the observed cation-exchange capacity. With these colloids it is highly probable that the lattice of these clays contains substantial amounts of tetrahedral Al. This may be due, in part at least, to the presence of hydrous mica in these samples. The work of Hellman, Aldrich and Jackson (1942) indicates that it may be difficult to distinguish sharply between hydrous mica and true montmorillonite. In any case, it is well established that the (001) spacings of so-called beidellite vary with the water content of the sample.

Since the exchangeable cations are located between lattice layers, it is probably immaterial, insofar as cation exchange is concerned, whether the lattice charge is occasioned by isomorphous substitution in octahedral or tetrahedral positions, provided the lattice layers expand in water sufficiently to make exchange possible. Therefore, any soil clay, the lattice of which shows marked expansion in water, will be designated montmorillonitic in this monograph.

From the foregoing, it must be evident that montmorillonite is the name of an isomorphous series, and that individual samples may vary considerably in chemical composition and in cation-exchange capacity. For this reason, and others that will be developed later, the cation-exchange capacity of inorganic soils cannot be definitely correlated with montmorillonite content.

Electron microscope studies by Ardenne, Endell and Hofmann (1940) and by Shaw (1942) indicate that, in dilute suspensions, single lattice layers of montmorillonite may be present. As the mineral occurs in the state of nature, the lattice layers appear to be fairly well oriented with respect to the *c* axis, but imperfectly with respect to the *a* and *b* axes. The lattice layers may be likened to loose leaves of paper, the flat sides of which face each other but with uneven edges. The binding power of exchangeable cations must be weak, since the layers are easily separated. Water molecules pass in between the plates freely, perhaps, in part at least, because of the tendency of the exchangeable cations to become hydrated. This gives rise to what has been called inner-crystalline swelling. If dried from benzene [Shaw (1942), Figure 14], the plates tend to orient more perfectly with respect to all axes.

Since the exchangeable cations occur on the planar surfaces of lattice layers, they are readily accessible to the ions of a solution and hence exchange takes place readily. The exchange reaction is rapid, resembling in this respect reactions in solution.

Hydrous Mica. It is well established that many soil types contain a clay mineral structurally similar to muscovite, but differing from muscovite in its lesser K content and greater cation-exchange capacity, the latter being intermediate between that of montmorillonite and muscovite. Different names have been given this mineral, *i.e.* X-mineral, glimmerton, hydrous mica and illite. Grim and his associates have investigated this mineral most thoroughly. However, not enough is known definitely about the mineral to justify an extended discussion. Its cation-exchange property can probably be explained very much as that of montmorillonite.

Hydrous mica is definitely a layer lattice mineral, but, unlike montmorillonite, it appears not to swell to an important extent in water. Adjacent lattice layers seem to be firmly held together somewhat as in the micas. The exchangeable cations probably lie relatively near the terminal edges of the plates and possibly in considerable part on the exposed planar surfaces of extremely thin crystals. This mineral is often found in soils associated with montmorillonite. Hendricks and Alexander (1939) suggested that these two minerals may be intergrown in the same crystal. There is need for a better understanding of the cation-exchange properties of hydrous mica.

Kaolinite and Halloysite. Kaolinite is a common constituent of well-leached soils in humid climates, and also of certain soils in relatively dry climates. Where the humus content is low, the cation-exchange capacity of such soils is also low. The same is true of pure kaolinite. The sequence of atomic planes in kaolinite is:

		Charges	
Si—tetrahedra	6 O ⁻²	-12	-28
	4 Si ⁺⁴	+16	
Al—octahedra	4 O ⁻² · 2(OH) ⁻¹	-10	+28
	4 Al ⁺³	+12	
	6 (OH) ⁻¹	-6	

The charges of the lattice being balanced internally, the crystal is unable to attract external cations, save by the negative charges of terminal O ions on the lattice edges. These forces are small in

number per unit weight, but probably numerous enough to account for the low cation-exchange capacity of kaolinite.

There is evidence that halloysite is a constituent of certain soils. Structurally, halloysite is similar to kaolinite, but instead of occurring as pseudo hexagonal plates, as in kaolinite, Shaw and Humbert (1941) showed that the crystals are lathe-shaped. The cation-exchange capacity of halloysite appears to be somewhat greater than that of kaolinite. It is possible that the exchangeable cations are attached to exposed O ions at the terminal edges of the lattice, as in kaolinite.

Other Minerals. Barshad (1944) and others have concluded that certain soils contain a cation-exchange mineral which closely resembles vermiculite, a Mg-aluminosilicate. Gruner (1934) showed that certain vermiculite-like minerals are composed of mixed layers of true vermiculite and hydrobiotite, while Hendricks and Jefferson (1938) concluded that in certain cases vermiculite is interleaved with chlorites. The differential thermal curves by Barshad made on certain fractions of prairie-like soils from California, including samples composed of relatively coarse-sized particles, were found to be quite unlike the curves for montmorillonite or mica, yet all these samples contained substantial amounts of exchangeable cations. A fully satisfactory explanation of the cation exchange property of these materials cannot be given now.

Joffe (1944) has also found that the cation-exchange material of certain soils from New Jersey is by no means confined to fine-grained particles, that is to the colloidal material. The relatively coarse-sized particles were found to undergo cation exchange to a pronounced degree. The mineralogical composition of this material has not been determined. Soils formed from green sands probably contain glauconite, a complex K-Mg-Al-Fe-silicate, which is responsible for their exchange property.

From the foregoing we can now affirm with considerable confidence that the inorganic cation-exchange material of soils is usually one or another or a mixture of the clay minerals montmorillonite, hydrous mica, kaolinite and halloysite. Montmorillonitic clay is the chief clay of soil types common to regions of moderate rainfall, while kaolinite is most common in the well-leached soils of humid climates. However, there are notable exceptions to this rule. The investigations referred to in the preceding pages leave no reasonable

ground for doubt that cation exchange in mineral soils is not primarily due to amorphous substances. It is explained on the basis of the structure and lattice composition of minerals (chiefly the clay minerals). The explanation does not involve any of the more or less vague ideas of previous periods. It rests on isomorphism in the case of montmorillonite and on unsaturated valencies at the terminal edges of the lattice layers of kaolinite and halloysite.

It should be pointed out that unbalanced charges at the terminal edges of montmorillonite also probably play a small part in its total cation-exchange capacity, but the area of terminal edges is small compared to that of flat surfaces, owing to the ratio of thickness, to length and breadth of the plates. Therefore, the contribution of terminal edges may be disregarded without serious error.

Number of Exchangeable Cations per Particle

Electron microscope photographs of montmorillonite by Ardenne *et al.* (1940) show many very thin plates with irregularly shaped edges. The thinnest plates were estimated to be about 10 Å thick and the length about 3000 Å. Shaw's (1941) electron microscope pictures show plates of various sizes and shapes, some of which were about 20 Å thick but commonly with irregular outlines. The average dimensions of the largest plates were approximately $1\mu \times 0.4\mu$.

According to Hofmann *et al.* (1933), the cell dimensions of montmorillonite are: $a = 5.095$ Å, $b = 8.83$ Å, $c = 9.6$ to 15 Å. From these data we can easily calculate the number of crystallographic units per lattice layer of any size. Plates $1\mu \times 0.4\mu$ would contain 888,786 cell units. If there is 0.33 negative charge per 12 oxygen, as is implied in Ross and Hendricks' formula, there would be 592,524 exchangeable monovalent ions per lattice layer. Plates $0.5\mu \times 0.2\mu$ would have 148,131 exchangeable monovalent cations, and plates $0.1\mu \times 0.04\mu$, 5925 per lattice layer. Assuming the same ratio of length to width for Ardenne's plates, that is 3000 Å \times 1200 Å, there would be 53,327 exchangeable cation per lattice layer. If the sample contains more than 0.33 exchangeable cation per 12 O, the number per lattice layer would, of course, be proportionately greater. These calculations show that montmorillonite contains a surprisingly large number of exchangeable cations per particle.

In making the foregoing calculations the plates were assumed to be rectangular. However, as stated above, the electron microscope

pictures show many particles with quite irregular outlines. Shaw presented two photographs of Wyoming bentonite, one dried from water suspension and the other from benzene. The former showed indistinct outlines, the latter fairly sharp boundaries with remarkably good orientation. As the mineral occurs in the state of nature it is probable that the crystals of montmorillonite are very far from regular geometrical forms. It is possible that this has something to do with the gelatinous nature of montmorillonite.

The investigations of Ardenne *et al.* indicate that the individual particles of montmorillonite from different sources differ considerably in shape and outline. This is consistent with the well-established fact that the physical properties of montmorillonite from different bentonites differ substantially. If similar differences characterize the montmorillonitic material of soils, their physical properties might vary accordingly. In any event, however much the shape and size of the particles may vary, and notwithstanding the extent to which isomorphism plays a part, the lattice structure does not vary greatly, as is shown by x-ray analysis.

The best evidence at present, then, is that the cation-exchange material of soils is composed of crystalline clay minerals and possibly other related minerals in certain cases. The crystals are undoubtedly platy. The minimum thickness of a plate is determined by the dimension of a lattice unit in the direction of the *c* axis, but the length, breadth and geometrical outlines appear to vary widely.

While x-ray analysis has afforded convincing evidence that the lattice units of montmorillonitic clay are well ordered, it does not follow that the chemical composition of all the lattice units, even in a given particle, is uniform. In fact, as implied already, calculations on the basis of mass analysis show that a variable percentage of the lattice cells are charged, while the remainder are electrically neutral. The evidence is that variations in lattice compositions among the cell units of a given particle and especially between the units of particles from different sources is an outstanding characteristic of montmorillonite and possibly of hydrous mica as well. But the dimensions of the cell units cannot vary beyond a narrow range. Otherwise the crystal would not be stable.

The exchangeable cations are located between lattice layers, and are held to the lattice by electrostatic attraction. Expansion caused

by the entry of water between lattice layers makes possible egress and ingress of cations. Consequently the cations are exchangeable.

The foregoing picture of the exchange material is a far cry from the older concepts and yet in certain respects it can be reconciled with the older concepts. The most important advances in recent years are: (1) The rationalization of the forces involved in cation exchange. (2) Explanation of the differences in cation-exchange power among soils. (3) The light thrown on general soil properties. The last named will be discussed in later chapters.

Chapter 3

Cation-Exchange Equations

At various times in the course of cation-exchange investigations, attempts have been made to show that the data can be expressed by an equation. Formerly Freundlich's (1909) adsorption equation was used. Later certain modifications of this equation were found that express the data more perfectly. Still later, equations derived from considerations of the law of mass action were developed, and finally equations have been derived from purely kinetic reasoning. As yet, general agreement is lacking as to which equation most correctly expresses cation-exchange relationships.

Adsorption Equations

Freundlich's Equation. Freundlich's equation, originally derived from the adsorption of a gas by a solid, is:

$$\frac{x}{m} = kp^{1/n}$$

as applied to cation exchange, x/m = amount of cations taken up from a solution at equilibrium with a given weight of soil, p = amount of the added cation remaining in solution, k and n = constants. By plotting $\log x/m$ against $\log p$ a straight line is supposed to result, the slope of which equals $1/n$ and the intercept on the ordinate equals $\log k$. Since this equation is the equation of a parabola, no adsorption maximum is indicated as the amount of replacing cation in the solution is increased indefinitely. However, since many investigations have shown that exchange capacity of every soil and clay is a finite quantity, it is evident that Freundlich's equation cannot express cation exchange over a wide range of concentration. Over a limited range of concentration it seems to apply fairly well.

Langmuir's Equation. Langmuir (1918) proposed an equation for the adsorption of a monomolecular layer of a gas by a solid. This equation, with appropriate redefinition of the quantities in-

volved, has been used to express the exchange adsorption of solution ions by soils. Writing the equation in a form comparable to Freundlich's equation, it is

$$\frac{x}{m} = \frac{k \cdot s \cdot c}{1 + kc}$$

where x/m = molecules of cations adsorbed, s = adsorption maximum, c = molecules of cations remaining in solution at equilibrium, and k = constant. This is the equation of an hyperbola, and hence it is not open to the same objection as Freundlich's parabolic equation. By plotting $c/x/m$ against c , a straight line is obtained, the slope of which represents $1/s$ and the intercept, $1/sk$. Thus the slope is dependent on the exchange capacity. Knowing the amounts of cations exchanged at two different concentrations of a given salt, it is possible in many cases to calculate the amount that will be exchanged with a third concentration.

Wiegner and Jenny's Equation. Wiegner and Jenny (1927) proposed a modification of Freundlich's equation which is:

$$a - c = k \left(\frac{c}{a - c} \right)^{1/p}$$

where $a - c$ = amount of cations adsorbed per gram of soil, c = concentration of original cations remaining in solution at equilibrium, a = initial concentration of the salt solution, k and p = constants.

Vageler's Equation. Vageler's (1930) equation is

$$y = \frac{s}{1 + \frac{c}{x}}$$

where y = amount adsorbed per gram of soil, x = equivalents of initial salt solution used per gram of soil, s = exchange capacity of soil, c = constant, called by Vageler the half value for the reason that when one-half of the exchangeable cations ($s/2$) have been replaced, $c/x = 1$.

All the foregoing adsorption equations are essentially empirical. They are based on the assumption that the adsorption of cations by exchange can be represented over a considerable range by means of an algebraic equation. In all cases the constants of the equations have no particular meaning in terms of the properties of the clay.

Moreover, no conclusions concerning the nature of the attractive force can be drawn from the fact that one or more of these equations are applicable to a given set of data.

Mass-Action Equations

The mass-action principle must be assumed to be operative in all chemical processes, since this principle is based ultimately on the law of conservation of energy. However, all mass-action equations for cation exchange in soils contain the tacit assumption that the adsorbed ions and the solution ions are definable and can be determined experimentally. On the basis of the idea of the diffuse double layer, the adsorbed ions and the solution ions are not definable as separate entities. As Davis (1945a) suggested, cation exchange, according to this picture, must be considered as merely the rearrangement of cations in the double layer, and not as a chemical reaction.

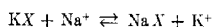
In the opinion of the author, the objections of Davis represent an inappropriately extreme view of soil-water systems as ordinarily encountered. It must be concluded on the basis of an abundance of experimental data that, in soil-water systems containing appreciable amounts of free electrolyte ($\sim 0.1 N$), the ion swarms must be essentially nondiffuse and the quantities "exchangeable ions" and "solution ions" are discrete and measurable. In the discussion to follow, it is assumed that systems of this type are involved, while at the same time it is conceded that certain isolated soil-water systems may exist (possibly systems of extremely low free-electrolyte content) concerning which the arguments may not be strictly valid.

Thus the exchange process is conceived as a chemical process, taking place between a solution phase and the exchange material. Knowing the amount of exchangeable cations on the original solid material and the composition of the initial solution, it is assumed that the amounts remaining in solution and in exchangeable form at equilibrium can be calculated from chemical analysis of the supernatant liquid or filtrate. Vanselow (1932b) showed that the relative activity coefficients of mixed electrolytes can be calculated from data obtained in this way.

When dilute salt solutions are used to bring about cation exchange, two kinds of complications may be involved. First, the analytical error may be relatively great; second, and perhaps more

important, hydrolysis, that is the replacement of exchangeable cations by H ions of water. By careful determination of changes in pH of the solution, suitable correction can possibly be made for hydrolysis.

Kerr's Equations. Conventionally, cation exchange between ions of equal valence is represented as follows:

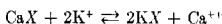


where X denotes exchangeable cations. Kerr's equation for this reaction is:

$$\frac{[NaX][K^+]}{[KX][Na^+]} = k \quad (A)$$

Gans (1913) and Rothmund and Kornfeld (1918) also developed mass action equations for cation exchange, both of which can be reduced to the same form as equation (A).

The exchange between divalent and monovalent cations may be represented as follows:



Kerr's equation for this exchange is:

$$\frac{[KX]^2[Ca^{++}]}{[CaX][K^+]^2} = k \quad (B)$$

As with all mass action expressions, the quantities in brackets should denote activities. However, since Gans (1913), Rothmund and Kornfeld (1918), and Kerr (1928a) (1928b) used concentrations in their equations, they tacitly assumed that activities are essentially equal to concentrations.

Vanselow's Equations. Since the activity coefficients of dilute KCl and NaCl are close to unity, approximately the same values for k will be obtained whether concentrations or activities for K^+ and Na^+ are used in equation (A) provided dilute solutions are used. However, this is not true of equation (B), since the activity coefficient of dilute $CaCl_2$ is substantially less than unity. Furthermore, the activity coefficient of $CaCl_2$ changes much more rapidly with changes in concentration than does that of KCl or NaCl.

The use of concentrations for the exchangeable cations in equations (A) and (B) implies that exchangeable cations act as if in true solution with an activity coefficient of unity. Vanselow (1932a)

recognized that the validity of this assumption is highly questionable. The activity coefficients of exchangeable cations in a salt solution-soil suspension are probably of a low order, and their values may be impossible of accurate experimental determination. As an approach to this problem in its bearing on the formulation of cation-exchange equations, it occurred to Vanselow that the activities of the exchangeable cations might be proportional to their mole fractions in the exchange material used, as is known to be the case with certain kinds of mixed crystals. If so, then KX in equation (A) will become

$$\frac{KX}{KX + NaX}$$

and NaX will be

$$\frac{NaX}{KX + NaX}$$

Substituting in equation (A):

$$\frac{\left(\frac{NaX}{KX + NaX}\right)[K^+]}{\left(\frac{KX}{KX + NaX}\right)[Na^+]} = \frac{(NaX)[K^+]}{(KX)[Na^+]} = k \quad (C)$$

Again brackets denote activities, while parentheses refer to concentrations. This equation differs from equation (A) only in that concentrations are used for exchangeable cations. However, the use of mole fractions in equation (B) for the exchange between divalent-monovalent ion pairs and activities for the ions in true solution gives the following:

$$\frac{\left(\frac{KX}{KX + CaX}\right)^2[Ca^{++}]}{\left(\frac{CaX}{KX + CaX}\right)[K^+]^2} = \frac{[Ca^{++}](KX)^2}{[K^+]^2 \cdot CaX(KX + CaX)} = k \quad (D)$$

This is Vanselow's equation for exchange between Ca ions and K ions. It differs from Kerr's equation (B) by the factor:

$$\frac{1}{KX + CaX}$$

Although Vanselow reported his analytical data as m.e. per liter, he used millimoles in his calculation. Vanselow pointed out that,

since the solutions used in his experiments were fairly dilute and of practically constant total ionic strength, the error caused by neglecting activities for the ions in true solution was fairly constant.

In a paper soon to be published, Vanselow will show that by using activities for the cations in true solution and mole fractions for the exchangeable cations, and correcting for concentration effects caused by the adsorption of water, the values obtained for (k) were remarkably constant over a wide range of concentration.

Kinetic Equations

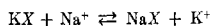
Gapon's Equation. Gapon (1933a) first developed an equation for the exchange between a liquid and a monomolecular layer of another liquid adsorbed on a solid. The amount of this kind of exchange is said to be determined solely by temperature. Representing the entire surface by F_0 , and the parts of the surface occupied by liquids C_1 and C_2 at equilibrium by F_1 and F_2 , respectively, Gapon arrived at the equation:

$$\frac{C_1 \cdot F_1}{C_2 \cdot (F_0 - F_2)} = k \quad (\text{E})$$

Gapon claims that the amount of a given liquid that will be taken up by a solid through exchange will be *proportional to the surface occupied by that liquid*. He also claims that cation exchange is analogous to the replacement of one liquid by another from the surface of a solid, and that cation-exchange capacity may be substituted for total surface.

Gapon applied his equation (E) only to the exchange between divalent and monovalent ions. It is of interest to see how it can be applied to the exchange between monovalent ion pairs.

Since F_0 (total surface) is assumed to be proportional to exchange capacity, applying equation (E) to the reaction

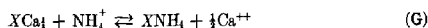


we get:

$$\frac{(\text{K}^+)(\text{NaX})}{(\text{Na}^+)(\text{KX})} = k \quad (\text{F})$$

This equation has the same form as Kerr's equation (A). Thus by quite different lines of approach, equations of the same form are obtained for the exchange between monovalent ion pairs.

For the exchange between cations of different valence, for example, Ca^{++} and NH_4^+ , Gapon writes the reaction as follows:



where X denotes exchangeable. Applying these quantities to equation (E) Gapon obtained:

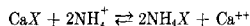
$$\frac{(\text{Ca}^{++})^{\frac{1}{4}}(\text{NK}_4X)}{(\text{NH}_4^+)(\text{NH}_4 \text{ ex. cap.} - \text{NH}_4X)} = k \quad (\text{H})$$

The cations found in solution are expressed as gram atoms per liter and the exchangeable cations as gram atoms per a given amount of soil.

By making

$$(\text{NH}_4 \text{ ex. cap.} - \text{NH}_4X) = X\text{Ca}_4$$

it is presumed that Gapon sought to avoid the necessity of taking the square root of $\text{Ca}X$. Certainly Gapon's equation (G) for the reaction between Ca-saturated soil and an ammonium salt is unusual to say the least, and no method of writing the reaction can possibly obviate the fact that two NH_4 ions are required to replace one Ca ion. Therefore, the reaction should be written:



Substituting these quantities in equation (E) gives an equation that is identical to Kerr's equation (B). Then assuming, as Gapon does, that the amount of a given cation taken up by exchange is proportional to the surface occupied by that cation, as in the displacement of one adsorbed liquid by another, and that cation-exchange capacity is proportional to total surface, then the quantities of exchangeable cations used in Gapon's equation should represent gram fractions rather than gram atoms.

Thus it follows that the essential difference between Gapon's and Vanselow's equations is traceable to Gapon's peculiar reaction equation, together with his neglect of the proportionality factor as regards the exchangeable cations.

It should be noted that, although equation (H) was derived from kinetic reasoning, Gapon considers this equation to be a mass-action expression.

Jenny's Equation. According to Jenny (1936), each exchangeable cation oscillates about the center of an electrical charge on the

surface of a particle. When a cation of a solution, normally in a state of thermal agitation, chances to pass between an exchangeable cation and the center of the electric charge, exchange takes place. The cation previously in solution becomes exchangeable, and simultaneously an exchangeable cation becomes a solution ion. Applying the probability law to this idea, Jenny developed a kinetic equation for the exchange between cations of equal valence. According to Jenny, cation exchange depends on chance—chance that the cations of the solution pass between the exchangeable cations and the surface of the solid. Jenny's equation follows:

$$W^2 \left(1 - \frac{V_w}{V_b} \right) - W(S + N) + SN = 0 \quad (\text{I})$$

where W = number of cations taken up or released at equilibrium, S = total number of exchangeable cations on the material used (cation-exchange capacity), N = number of electrolyte cations added, and V_w and V_b = oscillation volumes of the two kinds of cations when in the exchangeable form.

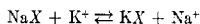
Since the ratio V_w/V_b is calculated, it is more convenient to write equation (I) in a transposed form.

$$\frac{W^2 - Ws - WN + SN}{W^2} = \frac{V_w}{V_b}$$

which is:

$$\frac{(S - W)(N - W)}{W^2} = \frac{V_w}{V_b} \quad (\text{J})$$

Applying this equation to the reaction:



we find:

$$\frac{(\text{K}^+)(\text{NaX})}{(\text{Na}^+)(\text{KX})} = \frac{V_w}{V_b} \quad (\text{K})$$

It is apparent at once that equation (K) is identical in form to equations (A), (C), and (F), where $V_w/V_b = (k)$. In other words V_w/V_b = the constant obtained by the ordinary mass-action equation.

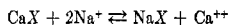
It is interesting to find then that exactly the same value is obtained for the exchange constant between ions of the same valence,

whether the equation is derived statistically or by application of the mass law.

Davis' Equation. On the basis of Jenny's oscillation volume concept, Davis (1945b) developed a probability equation for the exchange between monovalent and divalent cations. Davis first considered the probabilities that exchange will take place. On the basis of the results and by making certain assumptions, he finally arrived at the equation:

$$\frac{Zw \cdot (Nb)^{\frac{1}{2}}}{Zb \cdot (Nw)} = k \quad (\text{L})$$

where Zw and Zb = numbers at equilibrium of exchangeable monovalent w ions and divalent b ions, respectively, Nw and Nb = numbers of w and b ions in the free solution. Applying these quantities to the reaction:



we get:

$$\frac{(\text{NaX})(\text{Ca}^{++})^{\frac{1}{2}}}{(\text{CaX})(\text{Na}^+)} = k \quad (\text{M})$$

As Davis pointed out, this equation has the form of Gapon's equation (H). Davis claims that this equation will give a good constant only over a limited range of concentrations.

Both Jenny and Davis assumed that cation exchange depends on probability, and Davis strongly implied that the process is not chemical. However, Davis' equation gives a good constant only under certain conditions, namely, when the concentration of the solution does not vary widely and the amount of soil is kept constant. In contrast, Vanselow's equation gives a good constant over a wide range of concentration of solution and with widely variable amounts of soil, as any true mass-action equation should do.

Comments

It should be emphasized that the constancy of the calculated values, whichever equation is used, will depend in large measure on the accuracy of the analytical data. This means that the vast majority of published data on cation exchange need not be expected to give a good constant, owing to the fact that all known sources of error have not been eliminated in the techniques employed.

In view of the fact that by using activities for the cations in true solution and mole fractions for the exchangeable cations, Vanselow has shown that a good constant is obtained with his equation over a wide range of concentration of both solution ions and exchangeable ions, it is probable that Vanselow's equation is a correct mass-action expression. Should it be found, as Vanselow will suggest in his forthcoming paper, that the exchange between trivalent and mono-

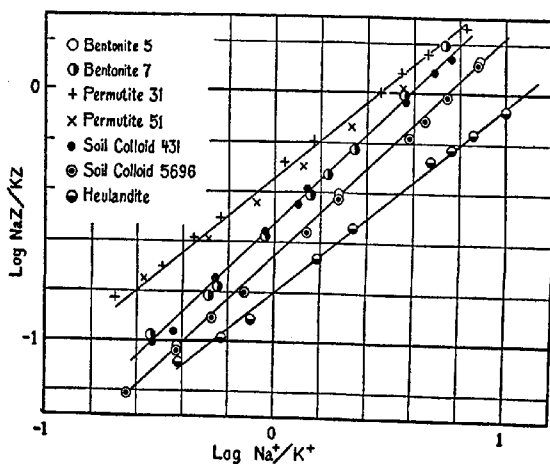


FIGURE 2. Equilibria in the Na-K exchange reaction of various aluminosilicates

Bentonite 5—Rosedale, Alberta, Canada

Bentonite 7—Goldfield, Nevada

Soil Colloid 431—Yolo soil, California

Soil Colloid 5696—Lahontan clay soil, Nevada

[Reproduced from Vanselow, 1932a]

valent cation pairs can also be expressed by his equation, then no reasonable ground for doubt will be left about the applicability of the mole-fraction principle to the exchange reaction. However, Marshall and Gupta (1933) expressed doubt about Vanselow's equation, and Davis (1945a) concluded that no mass-action equation is ever likely to be found that applies over a wide range of concentration.

Gapon (1933b) pointed out that his equation will not give a good

constant when applied to soil which contains two or more kinds of exchange material, for example, organic and inorganic. Vanselow showed that even the inorganic material of different soils and of bentonites from different sources give different exchange constants. This was well illustrated by plotting $\log \text{NaX/KX}$ against $\log \text{Na}^+/\text{K}^+$, as shown in Figure 2 which was reproduced from Vanselow's paper.

Thus we have strong evidence that the exchange activities of different soils and of different bentonites are not all alike. In the light of our knowledge that the clay minerals of soils differ both quantitatively and qualitatively, this is not surprising.

Thus it follows that none of the proposed equations need be expected to give a perfect constant over a wide range of concentration with all soils. But the lack of constancy of k , will not be due to the inapplicability of the mass law owing to diffuse double-layer effects or to the nonchemical nature of cation exchange. It can be accounted for simply by the lack of uniformity of the exchange material in the experimental sample.

Chapter 4

Principles of Cation Exchange

Rate of Reaction

Early in the history of cation-exchange investigations, the rate of the reaction was found to be rapid. Way recognized this fact in 1850. Subsequently, others have attempted to measure the rate, but the results have not been very successful owing to the great rapidity of the reaction. Gedroiz (1914) reported data obtained by shaking, for various periods of time, 100 grams of chernozem soil with 500 cc of *N* NaCl solution. After filtering, Ca was determined in the filtrate. The results are shown in Table 2.

These data show that contact between the soil and solution for the brief period of 5 seconds plus the time required to filter the solution (probably only a few minutes) was sufficient to establish equilibrium.

Gedroiz also made similar experiments using 50 grams of the same soil and 500 cc of *N* NH_4Cl . The results reported in Table 3 show that equilibrium was established by shaking only 3 minutes. It appears that a longer time of contact was required to establish equilibrium than with NaCl solution, but this was probably not significant.

Hissink (1924, p. 552) also investigated the rate of exchange. Twenty-five-gram samples of a clay soil from Holland were shaken with 250 cc of *N* NaCl for different periods of time. The results are shown in Table 4.

The foregoing results substantiate Way's conclusion that the exchange reaction takes place practically as soon as contact is established between the soil and solution. This is strong evidence in support of Hissink's (1922) conclusion that the exchangeable cations are held on the surface of the soil particles, as has already been brought out in Chapter 2. With soils, the cation-exchange material of which is largely montmorillonitic clay, as in chernozem soils, it is not difficult to see why the reaction should take place

rapidly. The exchangeable cations, being located on the surface of lattice layers, the so-called inner crystalline swelling makes possible the rapid passage of the solution into the spaces between lattice layers where exchange takes place.

However, Hissink found that Ca ions in the form of Ca-permutite are less rapidly replaced. By shaking 5 gram samples of Ca-permutite with 250 cc of *N* NaCl, he found the following amounts of Ca in

Table 2. Rate of Replacement of Ca^{++} by Na^+ [Gedroiz]

	CaO/100 gm
(1) Shaken 5 seconds—filtered immediately	0.1223
(2) Shaken 1½ minutes—filtered immediately	0.1222
(3) Shaken 5 minutes—filtered immediately	0.1210
(4) Shaken 3 minutes—filtered after standing 1 hour	0.1238
(5) Shaken 3 minutes—filtered after standing 24 hours	0.1220
(6) Shaken 3 minutes each day—filtered after standing 3 days	0.1234
(7) Shaken 3 minutes each day—filtered after standing 7 days	0.1218
(8) Shaken 3 minutes each day—filtered after standing 1½ months	0.1239
(9) Shaken 3 minutes each day—filtered after standing 3 months	0.1251
(10) Shaken 3 minutes each day—filtered after standing 14 months	0.1263

Table 3. Rate of Replacement of Ca^{++} by NH_4^+ [Gedroiz]

	CaO/100 gm
(1) Shaken 5 seconds—filtered immediately	0.1260
(2) Shaken 3 minutes—filtered immediately	0.1610
(3) Shaken 3 minutes—filtered after 5 hours	0.1629
(4) Shaken 3 minutes—filtered after 24 hours	0.1614
(5) Shaken 3 minutes each day for 3 days	0.1640

Table 4. Rate of Replacement of Ca^{++} by Na^+ [Hissink]

	CaO/100 gm
(1) Shaken 5 seconds	0.756
(2) Shaken 3 minutes	0.780
(3) Shaken occasionally for 1 day	0.780
(4) Shaken occasionally for 1 week	0.780
(5) Shaken continuously for 1 week	0.780

solution expressed as CaO: After 5 seconds, 2.3 per cent; after 3 minutes, 2.43 per cent; after one day, 3.15 per cent; and after one week, 3.22 per cent.

It is doubtful whether exchange equilibrium is established as rapidly with the hydrous mica-type of clay as with montmorillonitic clay, owing to the closeness of packing of the lattice layers of the former. Soil scientists should always bear in mind that no two soils are identical in all respects, and this probably applies to the cation-

exchange material. Differences in the amounts and relative proportions of the several components of soils account in considerable degree for the empiricism of soil science. Despite the great progress in our knowledge of soils, soil science is probably destined, unfortunately, to remain empirical to some degree, owing to the diversity and variability of the components.

Effect of Temperature

The temperature coefficient of cation exchange is generally small. Wiegner (1912) found a small negative temperature coefficient, while various other workers have found that the exchange reaction is accelerated somewhat by raising the temperature. Hissink (1922) and Kelley and Brown (1924) recommended that the soil extraction be carried out at approximately 70° on the ground that the exchange

Table 5. Influence of Ratio of Soil to Solution [Gedroiz]

Ratio	Ca Replaced (m.e./100 gm)
1:100	33.0
1: 75	32.4
1: 50	31.5
1: 25	29.5
1: 20	27.8
1: 10	25.5
1: 5	23.3

reaction is facilitated by raising the temperature. However, it now appears that the disadvantage of heating outweighs the advantage. Chapman and Kelley (1930) pointed out that heating above room temperature may increase the solubility of certain constituents and thus magnify the error which is always involved to some extent in cation-exchange determination. Further comment on this point will be made in connection with the discussion on methods, Chapter 6.

Ratio of Soil to Solution

Way pointed out that cation exchange is influenced by the ratio of the weight of soil to the volume of solution used. This has been verified by many other investigations. Gedroiz (1922) investigated this point and obtained the results shown in Table 5. In this experiment, 10-gram samples of chernozem soil were shaken with a series of volumes of 0.5 *N* NH₄Cl.

Effect of Concentration

Various workers have varied the concentration of the solution, keeping the weight of soil constant. Kelley and Cummins (1921) found, upon equilibrating a constant amount of Yolo soil with solutions of NaCl, that the replacement of Ca and Mg ions by Na ions increased as the concentration of the solution was increased (Table 6).

Table 6. Effect of Concentration of Solution [Kelley and Cummins]

Normality of NaCl	Cations Replaced (m.e./100 gm)	
	Ca	Mg
0.001	0.15	0.12
0.002	0.37	0.16
0.01	1.12	0.50
0.02	1.77	0.70
0.04	2.85	1.11
0.1	5.35	1.68
0.2	8.32	1.56

Table 7. Effect of Concentration of NH_4Cl [Gedroiz]

Normality of Solution	NH_4 Added (m.e./100 gm)	Cations Replaced (m.e./100 gm)		Ca:Mg
		Ca	Mg	
0.01	5	3.20	0.83	3.85
0.05	25	10.30	2.42	4.25
0.10	50	16.50	3.50	4.71
0.25	125	23.40	4.58	5.22
0.50	250	28.50	5.17	5.51
0.75	375	30.80	5.33	5.78
1.00	500	32.55	5.66	5.75
2.00	1000	35.55	5.83	6.10
4.00	2000	38.55	5.92	6.50

Gedroiz (1922, p. 18) shook 10-gm samples of chernozem soil to equilibrium with 50 cc of NH_4Cl solution of various concentration. The amounts of Ca and Mg replaced are shown in Table 7.

These results are of interest from three points of view. First, the amounts of both Ca and Mg replaced increased as the concentration of the solution was increased, but not in direct proportion to the concentration. For example, 0.05 *N* solution replaced 10.3 m.e. Ca plus 2.42 m.e. Mg, or a total of 12.72 m.e., whereas, 0.10 *N* solution replaced 16.5 m.e. Ca and 3.5 m.e. Mg, or a total of 20 m.e. Thus at relatively low concentration, doubling the concentration produced only about 60 per cent increase in the exchange. Sec-

only, the more dilute the solution, the higher the percentage of the NH_4 ions entering into exchange with divalent cations. Thirdly, the ratio of Ca to Mg replaced gradually increased with the concentration of the solutions. This last-named point will be referred to again later.

Gedroiz, as quoted by Gapon (1933b), showed the effects of concentration in another way. By keeping constant the absolute amounts of both soil and NaCl but varying the concentration of the solution, the results shown in Table 8 were obtained.

Table 8. Effect of Concentration of Solution [Gedroiz]
(100 gm soil + 100 m.e. NaCl)

NaCl Dissolved (liters)	Ca Replaced (m.e./100 gm)
1.0	16.5
2.5	14.5
5.0	12.9
10.0	11.1

Table 9. Effect of Concentration of Solution on the Replacement of Exchangeable NH_4^+ [Schachtschabel]

Solution Added (cc)	(normality)	Li	Per Cent of NH_4 Replaced by		
			K	Ca	Ba
400	0.0025	37.4	49.5	77.2	80.4
200	0.005	37.1	47.3	73.5	75.0
100	0.01	33.8	44.8	68.4	69.6
50	0.02	32.7	44.6	62.3	63.2
25	0.04	31.7	44.3	56.8	57.3
10	0.10	28.1	44.5	49.6	—

These data show that with constant amounts of both soil and NaCl present, the more concentrated the solution the greater the amount of exchange.

Schachtschabel (1940, p. 238) investigated the influence of concentration of Li, K, Ca and Ba ions on the replacement of NH_4 ions. One milliequivalent of both adsorbed NH_4 and of solution ions was used in each experiment, the latter being dissolved in 10 to 400 cc of H_2O , and the former adsorbed by montmorillonite. The equilibrated solutions were analyzed for NH_4 . In another experiment, one milliequivalent of Ca-montmorillonite was treated with a corresponding series of Ba or NH_4 solutions. The results are reported in Tables 9 and 10. The data (Table 9) show that a tenfold dilution of the K in solution (0.01 to 0.1 N) had no effect on the replace-

ment of NH_4^+ . At the highest dilutions, hydrolysis probably was a factor of some importance. The replacement with Li^+ was probably accompanied by more or less hydrolysis throughout. Over the range of concentration used in these experiments, the activity coefficients of K^+ and Li^+ were probably fairly constant. On the other hand, the activity coefficients of Ca^{++} and Ba^{++} are substantially increased by dilution. Accordingly, this may account for the results obtained in the replacement of NH_4^+ by Ca^{++} or by Ba^{++} .

The replacement of Ca^{++} by Ba^{++} (Table 10) was affected but slightly by dilution, while the replacement of Ca^{++} by NH_4^+ increased steadily as the concentration of the solution was increased.

Schachtschabel's results demonstrate quite conclusively, therefore, that the effects of concentration depend on what kind of cation is being replaced, and also on the nature of the replacing ion.

Table 10. Effect of Concentration of Solution on the Replacement of Exchangeable Ca^{++} [Schachtschabel]

Solution Added (cc)	(normality)	Per Cent of Ca Replaced by Ba NH_4	
400	0.0025	52.7	15.2
200	0.005	50.8	16.6
100	0.01	50.2	20.8
50	0.02	50.5	25.8
25	0.04	49.7	29.8
10	0.10	—	36.2

With cation pairs of similar replacing power and of the same valence, such as K^+ vs NH_4^+ or Ca^{++} vs Ba^{++} , dilution has relatively little effect on exchange, while with cations of different replacing power and different valence, for example, Na^+ vs Ca^{++} , or NH_4^+ vs Ca^{++} , dilution produces marked effect on exchange. A fully satisfactory explanation of these facts cannot now be given. Several factors were probably involved, such as variations in ion activities and ion hydration, etc.

Since soils commonly contain more than one kind of exchangeable cation and since the relative proportions of the adsorbed cations vary from soil to soil, the practical application of the foregoing results will be difficult.

Gedroiz' results, showing that dilution substantially decreases the power of monovalent cations to replace exchangeable Ca^{++} , are of special interest in connection with irrigated soils. The results suggest that the replacing effect of Na ions, as constituents of irri-

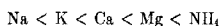
gation water, will fall off as the concentration of the solution decreases, and that with extremely dilute solution very little Na^+ will be taken up by the soil through exchange for Ca^{++} . As will be pointed out later, the same conclusion is drawn on the basis of the mole-fraction principle. On the other hand, it has been found that a very dilute solution of Ca^{++} will effectively replace Na^+ . The practical application of these facts will be more fully discussed in a later chapter.

Table 11. Exchange between NH_4 and Ca Ions [Vanselow]
(Equilibrium Approached from Opposite Directions)

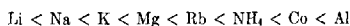
NH_4 Clay	Initially Present (m.e./liter)			In Solution at Equilibrium (m.e./liter)		
	Ca Clay	NH_4^+	Ca^{++}	NH_4^+	Ca^{++}	$\text{Ca}:\text{NH}_4$
<i>Shaken 5 hours at room temperature</i>						
19.68	0	0	20.06	12.68	7.47	1:1.70
0	20.00	20.12	0	14.37	5.91	1:2.43
<i>Shaken 7 hours at 75°</i>						
19.68	0	0	20.06	14.51	5.84	1:2.43
0	20.00	20.12	0	15.90	4.80	1:3.31

The Relative Replacing Power of Cations

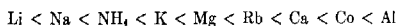
Way concluded that the replacing power of the common cations is:



Gedroiz (1922) reported the following, based on the replacement of Ca^{++} by 0.01 *N* solution of chlorides:



In the replacement of Ba^{++} by 0.1 *N* solutions, Gedroiz found:



Thus the relative replacing power of NH_4^+ seems to depend on what cation is being replaced and on the concentration, but this does not appear to be true of certain other cations.

Certain data reported by Vanselow (1932a) are of interest in this connection. He investigated the replacement of exchangeable NH_4^+ by Ca^{++} and of exchangeable Ca^{++} by NH_4^+ . In each case NH_4^+ and Ca^{++} were determined in the equilibrated solutions. The results are shown in Table 11.

Thus with equivalent amounts of Ca^{++} and NH_4^+ present, the relative amounts of Ca^{++} and NH_4^+ found in solution in each of these

experiments varied considerably, depending on which ion was originally adsorbed. Ca ions not only have considerably greater replacing power than NH_4 ions, but whichever is adsorbed tends to remain adsorbed. Vanselow and others have applied the term "hysteresis" to this phenomenon.

Liebig and Kelley (unpublished) obtained similar results by shaking to equilibrium 100 cc of CaCl_2 or NH_4Cl solution with equivalent amounts of NH_4^+ or Ca^{++} adsorbed on Yolo soil. Similar experiments were also made with Mg^{++} and NH_4^+ . The results are recorded in Table 12.

In contrast to the behavior of divalent-monovalent ion pairs, Vanselow (1932a) found that the exchange between Ca^{++} and Ba^{++} ,

Table 12. Exchange between Ca^{++} and NH_4^+ , and between Mg^{++} and NH_4^+

Ca Soil	Initially Present (m.e./liter)		NH_4^+	In Solution at Equilibrium (m.e./liter)		
	NH_4 Soil	Ca^{++}		Ca^{++}	NH_4	$\text{Ca}:\text{NH}_4$
2.94	0	0	2.94	1.01	1.97	1:1.97
0	2.90	2.90	0	1.19	1.79	1:1.50
Mg Soil	NH_4 Soil		Mg^{++}	NH_4^+	In Solution at Equilibrium (m.e./liter)	
	Ca^{++}	NH_4			Mg^{++}	$\text{Ca}:\text{NH}_4$
2.71	0	0	2.71	1.08	1.73	1:1.60
0	2.90	2.90	0	1.30	1.69	1:1.30

Table 13. Exchange between Ca^{++} and Mg^{++}

Ca Soil	Initially Present (m.e./liter)			In Solution at Equilibrium (m.e./liter)		
	Mg Soil	Ca^{++}	Mg^{++}	Ca^{++}	Mg^{++}	$\text{Ca}:\text{Mg}$
2.94	0	0	2.94	1.31	1.70	1:1.29
0	2.71	2.71	0	1.21	1.56	1:1.29

or between Ba^{++} and Cu^{++} gave approximately the same results whether approached from the right or the left. Liebig and Kelley (unpublished) obtained similar results with Ca^{++} vs Mg^{++} as shown in Table 13.

These data show that the hysteresis found between ions of different valence was not manifested between Ca and Mg ions. It will be noted that the ratio of total Ca to total Mg present was the same in each case, i.e. 1:1. The data also show that adsorbed Mg ions are more easily replaced than Ca ions. This fact will assume some pertinence in connection with the discussion which follows immediately.

Wiegner (1936) reported experiments on the replacement of Ca^{++} and NH_4^+ from mixed Ca- NH_4 -permutite, kaolinitic clay and bentonite. The materials were prepared in two different ways: (1) By

leaching Ca-saturated material with a solution of NH_4Cl and (2) by leaching NH_4 -saturated material with CaCl_2 solution. Both samples of each material thus prepared contained approximately 1 equivalent exchangeable Ca^{++} and 2 equivalents of exchangeable NH_4^+ . As prepared by the first-named method, the samples will be designated NH_4 -Ca material; and as prepared by the second method, Ca- NH_4 material.

Samples of these materials were shaken to equilibrium with a solution of NH_4Cl followed by determination of Ca in the solution. Other samples were shaken with CaCl_2 solution followed by a determination of NH_4 in the solution.

Expressing the maximum amounts replaced from each pair of samples as 100, the relative amounts found with the other of each pair are shown in Table 14.

Table 14. Replacement of NH_4^+ and Ca^{++} from Mixed Materials [Wiegner]

Samples	Solution Used	Ion Replaced	Permutite	Kaolinitic Clay	Bentonite
NH_4 -Ca material	CaCl_2	NH_4	100	100	100
Ca- NH_4 material	CaCl_2	NH_4	39.7	61.2	94.1
Ca- NH_4 material	NH_4Cl	Ca	100	100	100
NH_4 -Ca material	NH_4Cl	Ca	27.2	77.7	86.1

These data show that the replaceability of both NH_4 and Ca ions was influenced by the order in which they became adsorbed, the effect being most pronounced with permutite and least with bentonite.

Wiegner also found that similar differences in replaceability of the adsorbed ions were manifest over a concentration range from 5 to 50 m.e./liter. It is interesting to note, however, that the differences were least with the most dilute solutions. Wiegner also showed that permutite, saturated with two kinds of cations, exhibited the same type of phenomenon towards replacement by a third cation, Li^+ .

Wiegner proposed a purely mechanical explanation for the aforementioned results, namely, that the surfaces of the particles are irregular in outline, that is, they are made up of edges, ridges, summits, valleys, depressions and channels. When saturated with one kind of cation, some of the exchangeable cations will be located on edges, ridges and summits, and others in the valleys, channels, etc. He assumed that the former are more readily replaced than the

latter. Therefore, when two different samples are prepared, both containing two kinds of adsorbed cations, for example, Ca and NH_4 ions, one by replacing a part of the adsorbed Ca^{++} from Ca-saturated material with NH_4^+ , and the other by replacing a part of the NH_4^+ from NH_4 -saturated material with Ca^{++} , the cation used to effect the replacement will be the most accessible cation; that is, it will be located on the edges, ridges and summits. Although the ratio of Ca: NH_4 is the same in the two samples, the result will be that the relative replaceability of NH_4 and Ca ions will differ.

Wiegner explained the relatively great difference noted in the behavior of permutite and bentonite on the ground that the so-called meta-structure is much more highly developed in permutite than in bentonite.

If Wiegner's explanation is sound, it seems strange that the variations found should have been least with the most dilute solution. For we would expect just the opposite, since with a dilute solution the exchange would be expected to be largely confined to the most easily replaced ions. Furthermore, it seems probable that when a sample containing two or more kinds of adsorbed cations is allowed to stand, the adsorbed cations will tend to assume the most stable arrangement, regardless of the order in which they were introduced. If so, the differences found by Wiegner will be only temporary. This point could, it seems, be readily determined.

As shown above, the so-called hysteresis reported for certain ion pairs does not apply to the exchange between Ca^{++} and Ba^{++} , and Ca^{++} and Mg^{++} . Since Mg ions have considerably less replacing power than Ca^{++} , we would expect, in the light of Wiegner's explanation, to find evidence of hysteresis here also. Since this was not found, it seems that Wiegner's explanation is not entirely adequate.

In the opinion of the author, it is doubtful whether any purely mechanical or kinetic explanation of cation exchange will ever be found adequate to explain all the facts. The literature on cation exchange is replete with theories, one or another of which seems to explain certain experimental results well, but when applied to results obtained by other experimental methods and techniques, they either break down or else require substantial modification. As has been said of other questions, it is relatively easy to explain experimental results, provided the investigator is not hampered by too

many facts. The phenomena accompanying cation exchange are evidently complex and the serious student will be well advised to maintain a critical attitude towards theories in general.

In Chapter 2 it was suggested that the attractive forces on the surface of clay particles may be of different strengths. If so, some of the adsorbed cations should be more easily replaced than others. In other words, when Ca-saturated, some part of the adsorbed Ca ions will be held less strongly, and therefore be more easily replaced, than other Ca ions. This differentiation between the attractive forces, if real, is, of course, probably independent of meta-structural considerations, but might possibly be involved in the so-called hysteresis of Vanselow. However, granting that differences in attractive force are real, it seems probable that at true equilibrium the most stable arrangement would hold regardless of which cation was first adsorbed. As yet no satisfactory explanation of hysteresis has been proposed.

Influence of Kind of Exchange Substance

Schachtschabel (1940, p. 220) investigated the replacement of NH_4^+ adsorbed on a number of different kinds of substance. A quantity of each material containing one milliequivalent of adsorbed NH_4^+ was shaken to equilibrium with 100 cc of solution containing the desired cation as chloride. The relative order of replacing power was found to be as follows:

<i>Concentration of Solution</i>		<i>NH_4 Montmorillonite</i>
1		$\text{Li} < \text{Na} < \text{K} < \text{H} < \text{Rb} < \text{Mg} < \text{Ca} = \text{Sr} < \text{Ba} < \text{Cs}$
10		$\text{Li} < \text{Na} < \text{H} < \text{K} < \text{Mg} < \text{Ca} < \text{Sr} = \text{Ba} < \text{Rb} < \text{Cs}$
		<i>NH_4 Muscovite</i>
1		$\text{Li} < \text{Na} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Rb} < \text{Cs} < \text{K} < \text{Ba} < \text{H}$
10		$\text{Li} < \text{Mg} < \text{Ca} < \text{Na} < \text{Sr} < \text{Ba} < \text{Cs} < \text{K} < \text{Rb} < \text{H}$
100		$\text{Mg} < \text{Ca} < \text{Li} < \text{Sr} < \text{Ba} < \text{Na} < \text{K} < \text{H}$
		<i>NH_4 Permutite</i>
1		$\text{Li} < \text{Mg} < \text{Na} < \text{K} < \text{Ca} < \text{Sr} < \text{H} = \text{Rb} < \text{Cs} < \text{Ba}$
10		$\text{Li} < \text{Mg} < \text{Na} < \text{Ca} < \text{Sr} = \text{K} < \text{Rb} < \text{Cs} < \text{Ba} < \text{H}$
100		$\text{Mg} < \text{Li} < \text{Ca} < \text{Na} < \text{Ba} < \text{K} < \text{H}$

Thus it was found that the relative power of the several kinds of cations to replace NH_4^+ from a given substance depends to some extent on the concentration of the solution. This is probably traceable to the effect of concentration on ion hydration and ion activity.

However, with solutions of the same concentration the relative replacing power was markedly different between different kinds of adsorptive materials. For example, Mg ions have relatively strong replacing power for NH_4^+ adsorbed on montmorillonite, but weak replacing power with permutite. On the other hand, H ions replace NH_4 ions from montmorillonite only moderately, but with muscovite and permutite the H ion stands at the head of the list. Ca ions were found to be more effective than K ions with montmorillonite, but much less so with muscovite and permutite and this relation was not greatly altered by a 100-fold increase in the concentration.

From these results it would seem that, with solutions containing equivalent concentrations of Ca and K ions, the former will be taken up preferentially by montmorillonite and the latter by muscovite. Schachtschabel suggested a method, based on the foregoing results, for the determination of montmorillonitic and of mica-like clays when both are present in a given soil sample.

Hendricks and Alexander (1940) found that piperidine ions, $(\text{C}_5\text{H}_{10}\text{NH}_3)^+$, are taken up by montmorillonite in preference to H ions, while the opposite is true with hydrous mica. They also found that the difference between the adsorption of Ce ions and H ions by montmorillonite and hydrous mica is so marked as to be useful in semiquantitative estimation of those minerals.

As suggested above, the activity coefficients of Ca and Mg ions decrease with concentration much more rapidly than those of K and Na ions, and this fact probably accounts for the variations found by Schachtschabel with a given substance, but this could hardly account for the fact that Mg ions are much more energetic than Na or H ions in the replacement of NH_4 ions from montmorillonite and much less so with permutite. Not only was the relative order of these ions reversed, but the quantitative differences found by Schachtschabel were pronounced.

From the foregoing, it must be evident that our knowledge on cation exchange is far from complete. Almost any theory found applicable to one kind of material seems to require modification, sometimes substantial, when applied to other substances.

Other Possible Factors in Cation Exchange

Noting that among elements of the same valence the replacing power of cations increases with atomic weight, Gedroiz (1919) sug-

gested that atomic weight has something to do with cation exchange. Since the chemical properties of the elements are determined by the extranuclear electrons, it seems more probable that atomic number, rather than atomic weight is involved. However, the relationship is only qualitative. Other factors, such as ion size and ion hydration, seem to be involved also. As between cations of different valence, the relations are further complicated. In considering any of these factors, it is necessary to bear in mind that cation exchange involves both the uptake (*eintausch*) and the outgo (*austausch*) of cations. The hydration of adsorbed cations is almost certainly affected by interaction with the oppositely charged clay particles.

Table 15 sets forth the relationships between exchange power and the several factors referred to above. The data were taken from Gedroiz (1919) and refer to the replacement of Ba ions from Ba-saturated chernozem soil by 0.1 *N* solutions of chlorides.

Table 15. Replacement of Ba Ions in Relation to Various Factors [Gedroiz]

Ba Ions Replaced by: (m.e.)	Li	Na	NH ₄	K	Rb	Mg	Ca
Radius Å (dehydrated)	7.6	9.1	12.9	13.6	15.4	15.4	20.4
Radius Å (hydrated)	0.76	0.98	1.43	1.33	1.49	0.78	1.06
Atomic No.	3	7	—	19	37	12	20

Insofar as the replacement of Ba ions is concerned, Table 15 shows, that among ions of the same valence, a fair correlation between atomic number and radius of the ions in dehydrated form and an inverse correlation with ion radius in the hydrated form. As between cations of different valence these correlations break down. For example, the highly hydrated Mg and Ca ions have substantially greater replacing power than the less hydrated Li, Na and K ions.

When these data are considered in connection with the results of Schachtschabel, it is difficult to say just what is the most potent factor in cation exchange. It will be remembered that the relative order of replacing power of certain cations depends to a very large extent on the kind of adsorbing substance used. Therefore the kind of solid substance, as well as the nature of the cation, must be considered.

Effect of Hydration

Wiegner and Jenny (1927, p. 270) showed that the amount of Ca ions replaced from Ca-permutite by Na, K and Cs ions as chlorides

increased steadily as the alcohol content of the solution was increased. The results are reported in Table 16.

It is presumed that the degree of hydration of the ions in solution decreased roughly in proportion to the alcohol content of the solution. Since the cations adsorbed from the solution must have been equivalent to the Ca ions replaced, it appears that, as the water content of the solution, and therefore the degree of hydration of the solution cations, was decreased, the exchange was increased. Moreover, the replacing power of Na and Cs ions, although substantially unlike in purely aqueous solution was approximately the same in 80 per cent alcohol. It will also be noted that the absolute increases in replacing power of Na and K ions occasioned by adding alcohol to the solution was approximately the same, while the increases with Cs ions were substantially less.

Table 16. Relation between Cation Exchange and the Alcohol Content of the Solution [Wiegner and Jenny]

Alcohol Content (gm/100 gm)	(1 gm Ca-Permutite + 3.45 m.e. Chloride)		
	Na	Milliequivalents Adsorbed K	Cs
0	0.64	0.88	0.98
20	0.76	1.02	1.04
40	0.99	1.17	1.10
60	1.06	1.34	1.18
80	1.23	1.46	1.25

Wiegner and Jenny explained these results on the basis of ion hydration. Taking into consideration the fact that the sizes of these ions when completely dehydrated is $\text{Na} < \text{K} < \text{Cs}$, whereas, when fully hydrated, the diameter of Na ions is substantially greater than that of K or Cs ions, the explanation of Wiegner and Jenny is logical. However, despite the fact that Mg and Ca ions are more highly hydrated in aqueous solutions than Li and Na ions, Gedroiz (see Table 15) found that their power to replace Ba ions from Ba-saturated chernozem soil substantially exceeded that of Li and Na ions. It would be interesting to investigate the effect of ion dehydration on the replacement of ions of widely different sizes when adsorbed on different kinds of adsorbing substances.

It may be pointed out in this connection that the activity of ions dissolved in alcohol is probably quite different from that in water solutions. Some of this is due to ion hydration, but it may not be wholly due to hydration.

In the light of what is now known about cation exchange, the relative replacing power of the different cations apparently depends on the interplay of several factors: (1) The kind of material on which the exchangeable cation is held, (2) the degree of saturation with that cation, (3) the nature of the exchangeable cations associated with a given exchangeable cation, (4) the kind of liquid in which the exchange takes place. Other factors may possibly be involved also. It is evident, therefore, that cation exchange is far from being a simple process.

Table 17. Maximum Na Saturation Produced by Leaching with Na-Ca Salt Solution [Vanselow]

Total Conc. Ca + Na (m.e./liter)	Na in Leaching Solution (% of Total)							
	20	30	40	50	60	70	80	90
	Per Cent Na Saturation of Soil*							
1	0.25	0.40	0.65	0.80	1.05	1.37	1.98	3.09
5	0.52	0.90	1.35	1.90	2.42	3.27	4.65	7.30
10	0.80	1.30	1.90	2.65	3.50	4.75	6.70	10.60
20	1.25	2.00	2.85	3.85	5.11	6.92	9.67	15.25
30	1.60	2.50	3.65	4.85	6.45	8.70	12.23	19.00
40	1.80	2.90	4.25	5.75	7.58	10.20	14.25	22.25
50	2.00	3.30	4.75	6.50	8.60	11.54	16.10	25.20
60	2.25	3.65	5.30	7.20	9.50	12.77	17.80	27.70
70	2.50	4.00	5.75	7.85	10.30	13.80	19.40	29.80
80	2.70	4.35	6.20	8.50	11.17	15.05	21.00	32.20
90	2.85	4.65	6.65	9.10	11.86	15.96	22.50	33.90
100	3.05	4.90	7.05	9.65	12.60	16.90	23.60	35.70

* Calculated from unpublished data by the use of Vanselow's equation (D).

The Mole-Fraction Principle

A most fundamental advance in the chemistry of the exchange process was made by Vanselow (1932a) when he found that the activity of an exchangeable cation is proportional to its mole fraction in the sample. By means of this discovery it is now possible to describe the exchange process in terms of the mass law and of equilibrium constants in much the same way as ordinary chemical reactions are described. The importance of this work is the more apparent when it is recalled that for more than a century the treatment of the chemistry of soil processes in general, including cation exchange, has been largely empirical.

Vanselow also found that the mass action constants of different soils and also of bentonitic clays from different sources differ some-

what. This indicates that the activity of a given exchangeable cation depends on the kind of exchange material on which it is held. In other words, the nature of the surface forces on clays are not the same in all cases.

The very fact that the mole-fraction principle applies to cation exchange with clays denotes that the activity of a given kind of exchangeable cation diminishes as the percentage saturation with that cation decreases. This is consistent with the fact that the so-called availability of Ca in soils diminishes rapidly with base unsaturation. An acid soil may respond to liming even when the exchange material is 40 to 50 per cent Ca-saturated. On the other hand, plants are able to satisfy their K requirements from exchange material containing a low order of K saturation.

It follows then that the absolute replaceability of a given kind of exchangeable cation depends on the degree to which the exchange material is saturated with that cation. It also depends on the relative replaceability of the associated exchangeable cation. If the latter is more easily replaced than the former, the associated cation will be preferentially replaced when the material is treated with a solution of a third kind of cation.

The mole-fraction principle finds an important application in connection with the utilization of saline irrigation water in dry climates. By means of Vanselow's equation [Chapter 3, equation (D)] it is possible to calculate the maximum amount of cation exchange that will take place when irrigation water of almost any concentration or composition is applied over a period of years. As shown by Table 17, which was kindly furnished by Dr. Vanselow, a soil when irrigated with water low in salts will undergo cation exchange to a small degree only, even though Na ions constitute as much as 90 per cent of the total cations in the water. This means that the soil can never be caused to contain more than a low percentage of Na saturation by irrigation water of this kind no matter how much of it is applied. Since much of the available water in many localities contains more or less dissolved Na salts, this is an important point.

Thus it follows that the mole-fraction principle is far-reaching in its importance.

Chapter 5

Exchange Capacity and Kind of Exchangeable Cation in Various Soil Types

Although cation exchange is a universal property of soils, the extent to which different soils are able to exchange cations with solutions varies widely, ranging from a few m.e. to as much as 200 or more m.e./100 gm. The highest values are found among peaty soils. The exchange capacity of inorganic soils is rarely more than 75 m.e. and with the vast majority of inorganic soils it is substantially less than 50 m.e./100 gm.

In general, there is very little correlation between exchange capacity and content of fine-grained particles, that is, of the so-called colloidal material. To have ascertained that this was true would, no doubt, have troubled Way no end, since he was convinced that the clay material is the seat of the cation exchange and he was unaware of the variations in the types of clay. Now, however, we know that the different kinds of clay found in soils vary greatly in cation-exchange capacity. Some heavy clay soils have low, others high capacity, and the exchange capacity of certain sandy loam soils exceeds that of certain clay soils.

Generally speaking we can say that the exchange capacity depends on two variables, namely, the amount and the kind of exchange material present. Soils which contain montmorillonitic clay are generally relatively high in exchange capacity; those in which hydrous mica is the chief type of clay, are intermediate, while kaolinitic soils are usually low in exchange capacity. There are, however, some notable exceptions to this rule owing to the following facts: (1) The amount of clay is extremely variable, (2) The content of humus is likewise variable, (3) The silt and fine sand fractions of certain soils possess notable cation-exchange power. The exchange capacity of a kaolinitic soil rich in humus may exceed that of a montmorillonitic soil containing an equal amount of clay, but poor in humus. Hence the exchange capacity depends on the content and the kind of exchange material.

Neutral and Slightly Alkaline Soils

Calcium is the exchangeable cation present in the greatest amount in the vast majority of approximately neutral soils wherever they occur. The chernozems are notable examples of this class. Gedroiz (1916) showed that Ca comprises about 84 per cent of the total exchangeable cations in the Tula chernozem of Russia. Hissink (1922) reported Ca equal to 79 per cent of the total, as an average of 25 soils from Holland. Various determinations on chernozems and related soils of the United States have likewise shown a high percentage Ca saturation. Mg is commonly the next most abundant exchangeable cation, and exchangeable K and Na are usually pres-

Table 18. Approximately Neutral Soils

	Exchange Capacity (m.e./100 gm)	Ca	Per Cent of Total Mg	K	Na
Chernozem soil [Gedroiz, 1916]	56.1	84.3	11.0	1.6	3.0
Holland soils (Av. 25 samples) [Hissink, 1922]	38.3	79.0	13.0	2.0	6.0
Rothamsted soil (Av. 11 plots) [Page and Williams, 1925]	16.3	89.7	6.0	4.3	0
California soils (Av. 7 samples) [Kelley and Brown, 1924]	21.2	63.0	15.0	4.0	8.0
California soils (Av. 13 samples) [Martin, 1929]	20.3	65.6	26.3	5.5	2.6
India soils (Av. 11 calcareous soils) [Puri, 1936]	24.9	79.0	15.0	6.0*	

* Total K and Na.

ent in relatively small amounts. Generally speaking, calcareous soils, and soils from which CaCO_3 has but recently been removed by natural leaching, are relatively high in exchangeable Ca ions (see Table 18).

Exceptional Soils. The Yolo soils of California, and occasional small areas of other soil types in California, are exceptions in that they contain relatively much exchangeable Mg. Martin (1929) showed that the highly productive Yolo soil of the University Farm at Davis, California contains as much exchangeable Mg as exchangeable Ca. The writer has found other types of productive soil in California that also contain unusual amounts of exchangeable Mg.

Soils formed from serpentine rocks are sometimes found to contain much more exchangeable Mg than all other exchangeable cations combined. For example, a sample of heavy clay soil from Wooden Valley near Napa, California was found to be more than 90 per cent Mg-saturated. This soil is almost completely unproductive. Robinson *et al.* (1935) found that a considerable number of small areas of soils derived from serpentine, are characterized by high exchangeable Mg (see Table 19).

Other soils that contain relatively much exchangeable Mg will be discussed in the section on solonetz soil.

Table 19. Soils Derived from Serpentine Rocks

	Exchange Capacity (m.e./100 gm)	Ca	Per Cent of Total		
			Mg	K	Na
Maxwell soil, Wooden Valley, Calif.	46.2	4.2	93.0	0.8	2.0
(Av. 15 samples)	6.8	32.0	64.5	1.3	2.2
[Robinson, <i>et al.</i> , 1935]					

Base-Unsaturated (Acid) Soils

Base-unsaturated soils contain exchangeable H ions. The acids formed by biological agencies, or introduced into the soil as constituents of water, or otherwise, react with the exchange material, the H ions replacing metallic cations and producing base-unsaturated soil. The reaction is reversible, that is, metallic cations can replace H ions. This is precisely what takes place when lime is applied to acid soil.

Gedroiz (1924a) pointed out that as H ions replace metallic cations, the exchange material tends to become increasingly unstable. Especially is this true of montmorillonitic clay. Evidence in support of this is found in the fact that, regardless of the parent material, strongly leached soils tend to be kaolinitic. Many of these soils contain relatively little montmorillonite. This does not mean, however, that only kaolinitic soils can be acidic. The replacement of metallic cations by H ions tends to make any clay acidic. It suggests that upon replacement of a substantial percentage of the metallic cations by H ions, montmorillonite, formed at an earlier stage in the weathering process, gradually loses SiO_2 with the consequent conversion into kaolinite.

Since kaolinitic clay has low cation-exchange capacity, it follows then that inorganic base-unsaturated soils are likely to be relatively

low in cation-exchange capacity. This is often found to be true of the colloidal fraction of the soil as well as of the whole soil (see

Table 20. Colloidal Material of Acid Soils

Series and Location		Soil pH	Cation-Exchange Capacity (m.e./100 gm)
Cecil, Alabama [Kelley, et al., 1939a]	0-6"	5.50	22.0
Cecil, Alabama [Kelley, et al., 1939a]	8-15"	5.10	17.5
Cecil, Alabama [Kelley, et al., 1939a]	at 6'	5.10	16.5
Sierra, California [Kelley, et al., 1939b]	0-8"	5.80	22.7
Sierra, California [Kelley, et al., 1939b]	11-20"	5.50	19.6
Sierra, California [Kelley, et al., 1939b]	22-28"	6.00	16.0
Sierra, California [Kelley, et al., 1939b]	33-43"	6.60	16.4
Cecil, Virginia [Holmes and Edgington, 1930]	B	4.55	8.3
Cecil, North Carolina [Holmes and Edgington, 1930]	B	4.65	9.6
Cecil, Georgia [Holmes and Edgington, 1930]	B	5.30	7.3
Cecil, Georgia [Holmes and Edgington, 1930]	B	5.15	8.2
Cecil, Georgia [Holmes and Edgington, 1930]	B	5.20	7.5
Chester, New Jersey [Holmes and Edgington, 1930]	B	6.30	15.3
Chester, Pennsylvania [Holmes and Edgington, 1930]	B	6.70	18.4
Chester, Maryland [Holmes and Edgington, 1930]	B	5.07	26.9
Chester, Virginia [Holmes and Edgington, 1930]	B	—	20.6

Table 20). There are two world groups of soil that are preeminently base-unsaturated, namely, podsoils and the so-called lateritic soils. When freed from organic matter, the exchange capacity of these

soils is usually less than 10 m.e./100 gm. In addition, moderately leached montmorillonitic and hydrous mica soils, for example, the grassland soils east of the Mississippi River, also tend to be base-unsaturated. Such soils have been referred to by Gedroiz and others as degraded soils.

Many base-unsaturated soils are not merely low in exchange capacity; they are likely to be low in total exchangeable Ca. Puri (1936) showed that certain acid soils of India contain less than 1 m.e. of exchangeable Ca per 100 gm. Commonly, base-unsaturated soils are deficient in Ca from the standpoint of crop growth. It is largely for this reason, rather than because of low pH, that acid soils respond to liming.

There is abundant experimental evidence that exchangeable Mg and K ions are more easily replaced than Ca ions. For this reason it would be expected that the ratios of exchangeable Ca to exchangeable Mg and of exchangeable Ca to exchangeable K would increase as base unsaturation proceeds. However, after the early stages of normal weathering have passed, greater amounts of Mg and K ions than of Ca ions go into solution from nonexchangeable forms and this tends to complicate the picture. Gedroiz (1916) and Hissink (1922) pointed out that while a high percentage of the total Ca of soils is replaceable, this is true of neither Mg nor K. As regards K, this is a reflection of the fact that primary K minerals, such as the K feldspars and micas, are relatively resistant to weathering. As regards Mg, although many primary Mg minerals weather rapidly, Mg is a constituent of the secondary mineral montmorillonite and probably of hydrous mica also.

In general we can say that a high percentage of the Ca content of the clay minerals is exchangeable, and, with the exception of hydrous mica, the same is true of K, but only a relatively small part of the Mg is replaceable. Mg is a constituent of the lattice framework of certain clays, and it can be removed only as the crystal lattice undergoes alteration. However, this is apparently just what takes place as montmorillonite becomes base-unsaturated. Mattson *et al.* (1944) suggested that Mg ions derived from the decomposition of the clay gradually take up exchange positions. The data of Gedroiz (1916) are in harmony with this explanation. He found that the ratio of exchangeable Ca to exchangeable Mg was approximately the same in chernozem and in podsol.

The slow weathering of K minerals probably is responsible for the fact that base-unsaturated soils apparently contain small amounts of exchangeable K ions. Whether these ions are adsorbed on clay, or whether replaceable as constituents of feldspars and micas cannot now be decided. In any case the amount usually present is very small, but since the amount of exchangeable Ca ions tends to become less and less as base unsaturation proceeds, the ratio of Ca ions to K ions removed by replacing solutions may be even smaller in base-unsaturated than in base-saturated soils. Mattson *et al.* explained this fact on the basis of acidoid-basoid ratio as influenced by base unsaturation, together with the operation of the Donnan equilibrium principle.

Trivalent Cations. It is well-known that when base-unsaturated soils are extracted with a neutral salt solution, more or less, Al, Fe, or Mn commonly passes into solution. The question is, are these cations brought into solution through exchange or by the solution of some compound? Soil scientists are far from agreed on the answer to this question. Certain investigators hold that direct replacement of Al, Fe and Mn ions takes place. On the contrary, Gedroiz (1924a), Saint (1925), Kelley and Brown (1926) and others concluded that oxides or hydroxides of Al, Fe and Mn dissolve in the acid saline solution resulting from the replacement of H ions.

That trivalent cations are able to take part in exchange processes can hardly be doubted. The question is, do they ordinarily do so in natural soils? When it is recalled that $\text{Al}(\text{OH})_3$ is practically insoluble between pH 4.5 and pH 8.0, there is reasonable question as to whether any considerable concentration of Al^{+++} could exist in the soil solution of ordinary soils, and therefore whether Al^{+++} would be able to take up exchange positions like Ca and other cations.

As is well-known, soluble salts of Al hydrolyze. At concentrations likely to exist in the soil solution, simple salts of Al probably hydrolyze to a high degree. In such solutions Al probably exists chiefly as $\text{Al}(\text{OH})_3$, and hence the concentration of Al ions in the soil solution is extremely low. It is possible, however, that a low concentration of Al^{+++} , $\text{Al}(\text{OH})^{++}$, or $\text{Al}(\text{OH})_2^+$ may be present in the soil solution and that in the course of a long period of time the exchange material may take up more or less of these ions by exchange.

To prove or disprove that Al is or is not exchangeable in a given soil appears to be impossible at the present time. Kelley and Brown (1926) found that a neutral soil was made decidedly acidic by leaching it with 0.001 to 0.01 *N* AlCl_3 . At the same time the soil lost substantial amounts of exchangeable Ca and Mg ions. After having been leached with the AlCl_3 solution, the soil was found to contain practically no exchangeable Al as determined by the neutral *N* NH_4Cl method (see Table 21).

These results, however, do not prove conclusively that no exchangeable Al was introduced into this soil by leaching with AlCl_3 . It is possible that more or less Al ions were taken up by exchange for Ca and Mg ions upon leaching with AlCl_3 solution, and that when leached subsequently with NH_4Cl solution, NH_4 ions replaced Al ions, the latter being immediately precipitated in the soil mass as $\text{Al}(\text{OH})_3$.

Table 21. Effect of Leaching with AlCl_3 Solution on Exchangeable Bases and pH [Kelley and Brown, 1926]

Normality of AlCl_3	pH	Ca (m.e.)	Mg (m.e.)	Al (m.e.)	Exchange Capacity (m.e.)
0	6.95	21.8	6.1	0	27.3
0.001	5.96	18.0	5.4	0	27.2
0.002	5.65	16.9	3.8	0	27.2
0.004	5.05	15.0	3.8	0	26.1
0.010	4.94	10.1	2.7	trace	26.5

In any case, the fact that the pH of this soil was reduced from 6.95 to 4.94 by leaching with 0.01 *N* AlCl_3 , shows that H ions, originating from the hydrolysis of AlCl_3 , were largely responsible for the observed loss of exchangeable Ca and Mg ions.

✓Several investigators have reported that the Al content of the solution obtained by extracting acid soils with a neutral salt solution was almost equivalent to the titratable acid of the extract. If the Al found was brought into solution as Al^{+++} by exchange for cations of the salt solution, then it necessarily follows that practically no H ions were replaced. However, the pH of acid soils is commonly increased by treatment with a neutral salt solution. Since exchangeable Al ions, as such, can hardly be responsible for the low pH of acid soils, these soils must contain replaceable H ions. On the other hand, if we assume that the Al found in the extract, originated from the solution of Al-oxide or -hydroxide, then it would follow, in the case just referred to, that practically all replaced H

ions must have taken part in dissolving Al. Otherwise, the titratable acidity would not have been equivalent to the Al content of the extract.

Page (1926) suggested that upon the replacement of H ions, more or less of the exchange material decomposes with the liberation of $\text{Al}(\text{OH})_3$. In those cases where the Al content of the soil extract is approximately equivalent to the H ions of the extract, Page's suggestion would imply that for each H ions replaced one equivalent of Al ions passes into solution. This seems altogether improbable.

From the foregoing, it is evident that a definite decision cannot now be reached as to whether acid soils contain exchangeable trivalent cations, or whether some compound of these cations merely dissolves in salt solutions. In the opinion of the writer, both solution and replacement are probably involved. That soluble forms of Al actually occur in certain acid soils is indicated by the fact that dilute acetic acid (0.05 *N*) may bring substantial amounts into solution, as was shown by Burgess (1923).

Alkali Soils

Theoretically, it is possible to find a concentration and composition of soluble salts, which, upon accumulating in the soil, would produce no cation exchange whatever, but the probability is strong that wherever soluble salts have accumulated, as in arid regions, more or less cation exchange has taken place as a direct result of the soluble salts. Therefore, it is not surprising to find that the base status of the exchange material of alkali soils is different from that of normal soils. If the soluble salts are leached out after having accumulated, the soil may reflect that previous accumulation.

Soils which contain exchangeable Na in excess of that found in normal soils, are called alkali soils even when the soluble salts have been completely leached out. But insofar as the exchangeable cations are concerned, there is no sharp line between a leached alkali soil and a saline soil. Whatever exchange takes place must be produced while the soluble salts remain in the soil. In fact exchange takes place immediately upon the accumulation of soluble salts. Therefore, a given saline soil will contain fully as much exchangeable Na as the same soil after the soluble salts have been leached out. In fact it will usually contain a greater amount before than after leaching owing to the loss of exchangeable Na by hydrolysis and by exchange for some other metallic cation.

It follows then that the relative amounts of the several exchangeable cations of alkali soils are likely to be different from those found in normal soils. This fact was not recognized until Gedroiz began his important researches in Russia about 1910. A few years later, and before Gedroiz' results became known outside of Russia, de'Sigmond in Hungary, Hissink in Holland, and the writer and his colleagues in California, undertook the study of this problem. The results of all four of these widely separated centers of research have agreed in their essentials.

From the discussion in previous chapters, it must be apparent that the extent to which cation exchange has taken place in alkali soils, and the relative proportions of exchangeable cations that are

Table 22. Exchangeable Cations of Strongly Alkaline Soils

	Soil pH	Exchange Capacity (m.e./100 gm)	Ca	Per Cent of Total Mg	K	Na
Fresno sandy loam (Av. 4 samples) [Kelley, 1937]	9.8	4.5	18.7*	14.3	67.0	
Merced clay loam [Kelley, 1937]	10.0	18.9	0	0	5.0	95.0
Lahontan clay [Kelley, 1934]	9.0+	25.8	0	0	3.1	96.9
Indio sandy loam [Reitemeier, 1946]	8.3	8.0	32.5	7.5	5.0	55.0

* Total Ca and Mg.

found in the soil, depend on the concentration and composition of the soluble salts that have accumulated in the soil at some previous time. Since both the concentration and the composition of soluble salts vary widely in different localities, the base status of the exchange material also varies.

This is well illustrated by the data in Tables 22 and 23. The strongly alkaline soils (Table 22) contain exchangeable Na as the predominant cation, the amounts in the samples reported ranging from 55 to 97 per cent of the total. In all of these soils the amount of soluble Na salts present greatly exceeded that of all other kinds of salts.

In contrast to the strongly alkaline soils (Table 22), the more moderately alkaline saline soils reported in Table 23 present a very different picture. Despite the fact that these soils contained con-

siderable soluble Na salts, and some of them high concentrations, none contained especially high percentages of exchangeable Na. Five of the 7 samples contained no greater percentage of exchangeable Na than many nonsaline soils of dry climates. This is accounted for by the fact that, in addition to soluble Na salts, relatively high concentrations of soluble Ca or Mg salts were also present. The Fort Collins loam from Laramie, Wyoming, reported by Reitemeier, is especially interesting, in that the exchange material is about two-thirds Mg-saturated. This soil contains gypsum crystals. It also contains MgSO_4 which is highly soluble and Na_2SO_4

Table 23. Exchangeable Cations of Slightly Alkaline Saline Soils

	Soil pH	Exchange Capacity (m.e./100 gm)	Ca	Mg	Per Cent of Total K	Na
Merced clay [Kelley and Brown, 1924]	7.5	23.9	69.5	25.9	1.3	3.3
Willows clay [Kelley and Brown, 1924]	7.3	35.5	53.6	38.0	2.8	5.6
Holtville silty clay [Kelley, 1937]	7.5	17.6	90.0*		4.0	6.0
Imperial clay loam [Reitemeier, 1946]	7.45	26.1	69.0	23.0	1.0	7.0
Palouse loam [Reitemeier, 1946]	6.73	21.1	70.0	9.5	1.5	19.0
Regan loam [Reitemeier, 1946]	7.55	15.4	45.0	33.0	16.0	6.0
Fort Collins loam [Reitemeier, 1946]	7.70	16.2	10.5	66.7	2.5	20.3

* Total Ca and Mg.

which is also highly soluble, while gypsum is only moderately so. The soil solution, therefore, is largely a Mg-Na salt solution. Consequently the exchange material is relatively high in exchangeable Mg, moderately so in exchangeable Na, and unusually low in exchangeable Ca.

Reitemeier presented evidence that, upon leaching the Fort Collins soil, the relationship among the exchangeable cations would rapidly change owing to the removal of Mg and Na salts and the continued solution of CaSO_4 . When leached Ca ions brought into solution from gypsum will soon replace Na and Mg ions from the exchange material.

The soils reported in Tables 22 and 23 are good illustrations of the many alkali soils that have been investigated. They certainly show that, upon accumulation in the soil, soluble cations react with the exchange material, with the consequence that the base status of the exchange material becomes profoundly altered. An understanding of this fact and of the principles underlying the same is at the very core of the recent advances in our knowledge on alkali soils. Page and Williams (1926), Hissink (1932), and Kelley and Liebig (1934) have shown that the same type of reaction is involved when sea water comes into contact with soil. The actual base status of the exchange material at the moment of salt accumulation depends absolutely on the concentration and composition of the soluble salts.

Table 24. American Solonetz Soils

		Soil pH	Exchange Capacity (m.e./100 gm)	Ca	Per Cent of Total Mg	K	Na
Antioch, California [Kelley, 1934]	B ₁	7.1	25.0	41	49	1	9
Huerhuero, California [Kelley, 1934]	B	7.7	28.4	49	40	1	10
Aliso, California [Kelley, 1934]	B ₁	7.8	17.3	29	52	1	18
Cachuma, California [Kelley, 1934]	B ₁	7.0	29.2	27	67	1	5
Minnesota soils (Av. 7 samples) [Rost, 1936]	B	7.1	36.4	24.5	69.6	1.9	4

As the salts are leached out, changes in the exchangeable cations set in, owing to disturbances in the equilibrium between the soluble salts and the exchange material. If the soil contains solid phase CaSO_4 , leaching will rather quickly result in relatively high Ca saturation of the exchange material, irrespective of the composition of the soluble salts and of the base status before leaching. This is attributed to the continued solution of CaSO_4 .

Solonetz Soils

As used by Gedroiz (1928), the word solonetz refers simply to high percentage Na saturations; usually the content of soluble salts is low. According to Gedroiz, upon accumulation of soluble Na salts, Na ions replace other cations; leaching later removes the solu-

ble salts leaving exchangeable Na in the soil. As the natural leaching process continues, more or less exchangeable Na is replaced by H ions and then the term solod is applied. Solonetz soils are usually characterized by a peculiar type of morphology. In fact the classification is usually made on the basis of morphology.

Studies on American solonetz soils from several localities have shown relatively high exchangeable Mg but not especially high exchangeable Na (see Table 24).

Ellis and Caldwell (1935) reported certain soils of Canada, where the solonetz morphology is pronounced, which also contain relatively much exchangeable Mg. Frantzesson (1932) pointed out that certain solonetz soils of Russia are characterized by high Ca saturation. It appears, therefore, that the solonetz morphology is not always associated with a particular base status of the exchange material.

Chapter 6

The Determination of Exchangeable Cations

GENERAL PRINCIPLES

Regardless of the kind of exchange material being dealt with, whether soil or any other kind of substance, the quantitative determination of the exchangeable cations depends on the fulfillment of three conditions: (1) Complete replacement of all exchangeable cations by some cation which is not present in the sample, (2) accurate analysis of the solution obtained, (3) determination of, and suitable correction for, the cations that pass into solution (a) from soluble substances, or (b) by decomposition of some substance in the sample.

Experience has shown that the accurate determination of the truly exchangeable cations in the presence of soluble or decomposable substances is often extremely difficult. However, if the sample is free from both soluble and decomposable substance, the determination of exchangeable Ca, K, and Na can be made about as accurately as total Ca, K and Na. Statements in the literature to the effect that the determination is not highly exact have arisen primarily from two facts: (1) Complications growing out of the presence of soluble constituents, and (2) the use of different methods and techniques.

The *accurate* determination of truly exchangeable Mg in many soil types is more difficult than that of any other common cation. The apparent reason is that soils, especially if immature, contain Mg minerals which tend to decompose to some extent in the course of the determination. For example, it has been found repeatedly in the writer's laboratories that, after replacing Mg ions as completely as possible by leaching with a neutral Ca salt solution, the sample may still give up Mg to a neutral solution of NH_4 -acetate, and sometimes this continues throughout a prolonged period of leaching. A fully satisfactory explanation of this fact cannot be given now. It may be attributed to Mg minerals other than clay

minerals in the sample. Apparently pure montmorillonite may even contain intergrown layers of Mg compounds which slowly decompose. It is also possible that Mg ions occupying octahedral positions in the three-layer lattice of montmorillonite slowly pass into solution in salt solutions. Relatively immature soils act similarly. The results reported by Barshad (1946) show that certain California soils give up exceptional amounts of Mg to NH_4 acetate solution. The total equivalents of Ca, Mg, K, and Na ions found often exceed that of the NH_4 adsorbed substantially.

One of the most potent and important factors in the determination of exchange capacity is the pH of the replacing solution. Moreover, it is difficult to effect complete replacement of exchangeable divalent cations by Na or Li ions. For this reason, exchangeable Ca, as determined with Na or Li salts, is likely to be somewhat low.

With approximately neutral, noncalcareous soils from humid climates, solubility and decomposition effects can usually be disregarded without serious error (although there are exceptions to this rule), but many soils of dry climates contain amounts of soluble cations which cannot be ignored. Obviously, cations dissolved in the soil moisture, or present in a form which merely dissolves in the solution used for the determination, are not brought into solution from exchangeable forms. Therefore, the amounts of such cations must be subtracted from the totals found in the final solution. The determination of soluble cations, however, is sometimes fraught with considerable uncertainty.

The cations dissolved in the soil moisture are presumably in approximate equilibrium with the exchange material, as well as with the undissolved salts, but this equilibrium is easily disturbed. Upon adding water, as in the determination of soluble salts, the equilibrium is likely to be shifted in the direction of increased amounts of soluble Na. This effect is usually unimportant with nonsaline soils, but it may be considerable with saline or alkali soils. Eaton and Sokoloff (1935) showed that with certain alkali soils, soluble Na increased as the ratio of water to soil was increased. This was verified by Kelley (1939) and by Reitemeier (1946). There are three reasons for this fact, one or more of which apply to many soils of dry climates: (1) Exchangeable Na tends to be released from the adsorbed state by hydrolysis, particularly if the percentage of Na saturation is relatively high; (2) the relative replacing power of monovalent and

divalent cations is influenced markedly by concentration; (3) Ca ions derived from the solution of salts of low solubility, such as CaCO_3 and CaSO_4 , tend to replace exchangeable Na. The net result of these processes is that soluble Na is increased at the expense of exchangeable Na by merely diluting the soil solution.

A similar situation may be encountered as between Ca and Mg. Reitemeier (1946) reported results with one soil in which the ratios of soluble Ca to soluble Mg and of exchangeable Ca to exchangeable Mg were reciprocally affected to a marked degree by adding water to the sample. This soil contained considerable sulfate. The explanation appears to be as follows: MgSO_4 is highly soluble, whereas CaSO_4 is much less so. At a low moisture content, the ratio of dissolved Ca to Mg is low, and accordingly the ratio of exchangeable Ca to exchangeable Mg is also low. Upon adding water, additional amounts of CaSO_4 dissolve which increases the ratio of dissolved Ca to Mg. The consequence is the equilibrium between dissolved and exchangeable Ca and Mg is disturbed; exchangeable Mg ions are replaced by Ca ions. The soil will then contain additional amounts of exchangeable Ca and proportionately less exchangeable Mg.

From the foregoing it follows that the determination of soluble cations should be made with the lowest water-soil ratio possible. Further reference to this point will be made later in this chapter.

If CaCO_3 is the only carbonate of low solubility present, correction can be made for the carbonate that dissolves in the salt solution used. Unfortunately, other carbonates are also likely to be present, especially in alkaline saline soils. With such soils it is difficult to determine exchangeable Ca and Mg individually. CaSO_4 is also likely not to be the only sulfate present. Moreover, SO_4 ions, adsorbed on colloidal constituents, may be replaced by OH ions. Hence, SO_4 determination cannot be relied on as a basis for calculating the content of CaSO_4 .

When completely free from carbonate and sulfate, many non-saline soils of dry climates also give up to a salt solution substantially more total cations than they adsorb by exchange from the solution. This is probably due in considerable part to the solution of partially weathered silicates.

It follows, then, that it may be difficult to distinguish sharply between exchangeable and soluble forms. This is particularly true

of Ca and Mg in saline soils; it may also apply to K and Na to some extent.

In any case, the amount of NH_4 adsorbed upon leaching the soil thoroughly with a neutral normal ammonium salt solution is, with the possible exception of soils rich in humus, probably as accurate a measure of cation-exchange capacity at pH 7 as can be found. Comparison of this quantity with the sum of all the cations that are brought into the ammonium salt solution will indicate at once whether or not important amounts of one or more kinds of cations have been brought into solution by some process other than by exchange. Fortunately cation-exchange capacity at pH 7 can be determined with fair accuracy both in the presence and the absence of soluble or decomposable substance.

It is important to emphasize the fact that the exchangeable cations can be replaced by H ions as well as by NH_4 or metallic cations. For this reason the pH of the salt solution used in the determination may have significant influence on the amount of NH_4 or metallic cations that are adsorbed through exchange. Since the amount of NH_4 adsorbed is widely used as a measure of cation-exchange capacity, the salt solution used should be neutral. Further, the liquid used to leach out the occluded ammonium salt after replacing the original exchangeable cations should be both neutral and free from any cation that is capable of replacing NH_4 ions. Chapman and Kelley (1930) showed that by leaching with only slightly acid alcohol, or with alcohol neutralized with NaOH, a considerable error was introduced. However, this error can be largely avoided by neutralizing the alcohol with NH_4OH . When the occluded ammonium salt is leached out with distilled water, Kelley (1927) showed that a substantial amount of absorbed NH_4 may be lost by hydrolysis.

As Mattson (1931a, 1931b) emphasized, exchange capacity denotes the total amount of cations that can be exchanged under a given set of conditions, and not necessarily the amount that could be exchanged under other conditions. If the determination is made with a *neutral* solution of a given salt, the cation-exchange capacity found may be significantly less than when determined with an *alkaline* solution of the same salt. Hence, the pH of the solution should always be stated. As frequently given in the literature, the expression "cation-exchange capacity" has no definite meaning.

The methods and techniques used have varied considerably, including the use of different kinds and concentrations of salts, and variations in pH.

The exchange reaction is subject to the principle of chemical equilibrium. Therefore, the cations brought into solution by exchange, or by any other process, must be removed from contact with the soil; otherwise the replacement will not be complete. Hence, the sample should be leached with a neutral salt solution until the solution passes through unchanged.

Analysis of the extract of the soil is facilitated by removal of the salt used to effect replacement. Since ammonium salts can be readily decomposed or volatilized, and since exchangeable NH_4 is usually not an important constituent of soils, the replacement of the cations is most commonly brought about with an ammonium salt solution. The exchange capacity of humous soils can probably be best determined with a Ba salt solution owing to the fact that NH_4 humus is somewhat soluble in NH_4 salt solution.

METHODS

Literally dozens of methods, many of which differ but slightly, have been proposed for this determination. All of them involve the replacement of the exchangeable cations followed by analysis of the resulting solution. No good purpose would be served by reviewing all these methods. Only those of historic interest and of greatest usefulness will be outlined. Furthermore, since this monograph is not a treatise on analytical chemistry, the details of the analytical procedure required, once the exchangeable cations have been brought into solution, will be omitted.

Pillitz reported a method for determining cation-exchange capacity in 1875. It involved leaching a weighed sample of soil with approximately 1.4 *N* NH_4Cl until a small amount of the leachate gave no residue upon evaporation and ignition. Then the loss of *N* sustained by the solution was determined. From the results, the NH_4 absorbed by the soil was calculated. This method obviously necessitates the accurate standardization of the NH_4Cl solution, and the avoidance of evaporation of the solution during the leaching process.

In 1887 *Kellner* proposed what was probably the first allegedly quantitative method for the determination of both exchangeable

metallic cations and exchange capacity of the soil. With this method 25 grams of dry soil is shaken with saturated NH_4Cl solution and then allowed to stand quiescent. When the soil particles have completely settled, the clear supernatant solution is decanted off, fresh NH_4Cl solution is added, and the aforementioned processes are repeated 15 to 17 times, or until the supernatant solution is free from metallic cations. The decanted solutions are combined and analyzed for Ca, Mg, K, Na and NH_4 . The amount of NH_4 found subtracted from the NH_4 content of an equal volume of the original NH_4Cl solution is supposed to equal the exchange capacity. Apart from tediousness, the amounts of exchangeable metallic cations found by this method cannot be highly accurate with many soils, since no provision is made for the determination of soluble cations. Neither is it likely that cation-exchange capacity thus determined will be highly accurate for the reason given already and also because of the difficulty of accurate determination of NH_4 in saturated NH_4Cl solution.

Although Henneberg and Stohmann pointed out in 1858 that water-soluble salts and CaCO_3 , when present in the sample, complicate the determination of the stoichiometry of cation exchange, Gedroiz (1918) was the first to develop special methods for the determination of exchangeable cations in different kinds of soils.

Nonsaline Soils Free from CaCO_3

Gedroiz NH_4Cl Method. In his early investigation Gedroiz (1912, 1914, 1916) used a slightly modified form of Kellner's (1887) method. He showed in 1918 that approximately as complete replacement of exchangeable cations can be effected with N NH_4Cl as with more concentrated solutions. In addition to the tedious decantation procedure of Kellner, Gedroiz suggested a leaching procedure as follows: 25 grams of dry pulverized soil is first shaken with 250 cc of N NH_4Cl ; then the sample is transferred to a filter and leached with N NH_4Cl until the last portion of leachate gives no test for Ca. Metallic cations are then determined in the leachate.

Gedroiz HCl Method. Recognizing that exchangeable metallic cations can be replaced by H ions, Gedroiz (1923) proposed the HCl method. By this method 25 grams of dry soil is leached with 0.05 N HCl , using essentially the same technique as with NH_4Cl solution. The acid leachate is, of course, analyzed for metallic cations.

Kelley and Brown's NH_4Cl Method. In view of the fact that NH_4Cl is an acid salt, Kelley and Brown (1924) proposed the following method: Twenty-five grams of well-pulverized air-dry soil is shaken with *N* NH_4Cl neutralized to pH 7 with NH_4OH^* . The sample is then allowed to stand several hours at 70° , after which the contents of the flask are thrown onto a filter and the soil is leached with neutral *N* NH_4Cl until one liter of leachate is obtained. The filtrate is evaporated to dryness in the presence of strong HNO_3 in order to decompose NH_4Cl . The residue is brought to dryness two or three times in the presence of strong HCl . After filtering out the small amounts of SiO_2 , Ca, Mg, K and Na are determined.

The NH_4 adsorbed from NH_4Cl is determined in the soil left on the filter by distillation after first leaching out the occluded NH_4Cl . Kelley and Brown (1927) showed that more or less adsorbed NH_4 may be lost by leaching with distilled water, presumably through hydrolysis. However, this loss can be avoided by using either neutral methyl or ethyl alcohol. The adsorbed NH_4 thus determined is a fairly accurate measure of cation-exchange capacity at pH 7.

The important feature of this method, which seems to have been generally overlooked, is the neutralization of the NH_4Cl solution. By using neutral *N* NH_4Cl the exchangeable cations are replaced very largely, if not completely, by NH_4 ions; whereas, if an acid solution of NH_4Cl is used, H ions as well as NH_4 ions will take part in the replacement, in which case the adsorbed NH_4 will be somewhat less than the true exchange capacity at pH 7.

Ammonium Acetate Method. In 1913 Prianishnikov employed ammonium acetate in the determination of exchangeable K. More recently Schollenberger (1927) (1930) called attention to the advantages of ammonium acetate. It is now widely recognized that ammonium acetate is well suited to this determination. Schollenberger and Simons (1945) gave a detailed outline of the technique which they have found useful with this method. However, the exact technique is not the important point. What is important is to leach with approximately normal neutral ammonium acetate until the exchangeable cations are completely replaced by NH_4 ions.

*In their original publication Kelley and Brown inadvertently left out reference to the neutralization of NH_4Cl . However, this omission was corrected in later publications [Kelley and Brown (1926, p. 295); Kelley (1929, p. 1024)].

The replaced H ions may be determined by electrometric titration of the leachate and the metallic cations by analysis of the leachate. The adsorbed NH_4 (exchange capacity) is determined in the same soil sample by distillation or aeration in the presence of an alkali after having first removed occluded ammonium acetate by leaching with neutral methyl or ethyl alcohol. If the soil contains much organic matter, more accurate results may be obtained by aeration, if properly carried out, than by distillation, since certain organic nitrogen compounds are converted into NH_3 by distillation in the presence of MgO or other alkaline substances.

Soils Containing CaCO_3

Gedroiz' Method. The presence of CaCO_3 in the sample does not interfere with the determination of exchangeable Mg, K, and Na, but the solubility of CaCO_3 must be taken into account in calculating the exchangeable Ca. According to Gedroiz (1918), exchangeable Ca can be determined by subtracting from the Ca found in NH_4Cl leachate, an amount of Ca equivalent to CaCO_3 dissolved. He arrived at this quantity by determining CaCO_3 in the sample before and again after leaching out the exchangeable cations. By this method the sample is leached until the Ca content of the leachate becomes constant. As stated above, it is necessary to continue the leaching until practically all CaCO_3 has been dissolved; otherwise not quite all the exchangeable Ca will be replaced.

Hissink's Method. Owing to the fact that CaCO_3 is less soluble in NaCl than in NH_4Cl , Hissink (1922) recommended the use of N NaCl . Twenty-five grams of soil is leached with N NaCl to one liter, after which the leaching is continued until a second liter of solution passes through. The Ca content of the second liter is subtracted from that of the first liter on the theory that (1) all exchangeable Ca will be replaced by the first liter of NaCl , and (2) equal amounts of CaCO_3 will be dissolved by each liter of the solution. In other words, the second liter will contain Ca derived solely from CaCO_3 , whereas the first liter will contain an equal amount of Ca from CaCO_3 and also the whole of the exchangeable Ca.

Chapman and Kelley (1930) showed that Hissink's assumptions may not correspond to the facts. They found that as long as the solution in contact with the soil contains dissolved Ca ions, the soil

will not be free from exchangeable Ca ions. Moreover, if the original content of CaCO_3 is low, the first liter of NaCl solution may dissolve practically all CaCO_3 present, in which case the second liter will be practically free from Ca. In addition it is difficult to effect complete replacement of all exchangeable Ca ions by means of Na ions. For these reasons Hissink's method is likely to give results which are somewhat less than the total exchangeable Ca.

Puri's Method. Puri (1936) proposed the following method for the determination of exchangeable Ca in calcareous soils. Ten grams of soil is shaken for 2 hours with 200 cc of a solution 0.1 *N* with respect to Na_2CO_3 and *N* with respect to NaCl, filtered and the CO_2 content of the solution is determined. The loss in CO_2 sustained by the solution is equivalent to the exchangeable Ca. CaCO_3 is insoluble in this solution and the exchangeable Ca ions that are replaced by Na ions immediately precipitated as CaCO_3 .

Puri also found that exchangeable Ca can be determined in calcareous soils by the use of a solution containing a definite mixture of K- or NH_4 -oxalate-acetate-carbonate. CaCO_3 is practically insoluble in this solution and the decrease in oxalate ion content of the solution is considered to be equivalent to exchangeable Ca. Puri further states: "Soil containing gypsum requires a preliminary treatment with an excess of BaCO_3 when the CaSO_4 is converted to BaSO_4 and CaCO_3 ". If alkali salts are also present, it is necessary to leach out the same with alcohol before any of the above solutions is added.

Tjurin's Method. Tjurin (1927) recommended the following method for the determination of exchangeable Ca and Mg ions in calcareous soil: Ten grams of soil is leached with *N* NaCl solution until the final leachate contains Ca + Mg equivalent to its content of $\text{CO}_3 + \text{HCO}_3$. The equivalents of Ca + Mg removed in the combined leachate less the equivalents of $\text{CO}_3 + \text{HCO}_3$ represents replaceable Ca + Mg.

Mehlich's Method. Mehlich (1942) suggested that 0.2 *N* BaCl_2 buffered to pH 8.2 with triethanolamine may be useful in the determination of exchangeable cations and cation-exchange capacity of calcareous soils. CaCO_3 is practically insoluble in this solution. The cations removed from the soil by leaching with this solution are considered as having been replaced by Ba ions; consequently the Ba lost from the solution is a measure of cation-exchange ca-

capacity. Sulfate must be absent; otherwise, the results will be too high.

With soils which contain MgCO_3 in addition to CaCO_3 there is no known method by which exchangeable Ca or Mg can be determined directly. As will be shown in the next section it is possible to determine exchangeable Ca and Mg in such soils, collectively.

Saline Soils

The accurate determination of exchangeable cations of all kinds in saline soils is perhaps more difficult than with any other kind of soil. Such soils frequently contain carbonates of both Ca and Mg; they may be free from carbonate, neutral or strongly acidic. In many cases CaSO_4 is a constituent, and the total amount of soluble salts and the relative proportions of different kinds of salts vary widely in saline soils. Consequently, the determination of the several kinds of exchangeable cations will probably be merely approximate.

In 1925 Kelley and Brown stated: "In view of the complexity of the system involved in soils; the ready reactivity and lability of some of the constituents; the presence in alkali soils of relatively high concentrations of soluble salts, *whose determination may affect the exchangeable constituents to some extent*; and the errors due to solubility effects, it is *not reasonable to expect highly accurate results with any method*". Fortunately, no convincing evidence has yet been obtained showing that approximate results will not suffice, insofar as the solution of practical soil problems is concerned.

Gedroiz' Method. Gedroiz recommended the removal of soluble salts by leaching with water, after which the exchangeable cations are determined as with nonsaline soils. With soils free from gypsum, Gedroiz held that leaching with water does not produce any important change in the exchangeable cations. However, from what has already been stated, it is practically certain that Gedroiz was mistaken about this. If the soil contains CaCO_3 in addition to soluble sodium salts, leaching with water will assuredly bring about the replacement of more or less exchangeable Na by Ca ions derived from the solution of CaCO_3 .

Kelley and Brown's Method. Kelley and Brown (1925) showed that calcareous soils containing relatively much exchangeable Na can be caused to lose a large part of their exchangeable Na, and to gain a corresponding amount of exchangeable Ca, by leaching with

distilled water. Furthermore, mere dilution with water, if the soil contains both soluble monovalent and divalent cations, disturbs the equilibrium between exchangeable and soluble cations.

It follows, then, that the base status of the exchange material may be altered to some extent in the very process of determining the soluble salts, as was pointed out by Kelley and Brown in 1925. However, some allowance must be made for the soluble cations, the amount of which may exceed the total of all exchangeable cations present.

Kelley and Brown (1924, 1925) determined the cations in 1 to 5 water extracts of the soil, the amounts found being considered the soluble cations. Eaton and Sokoloff (1935), Kelley (1939) and Reitemeier (1946) have shown, however, that this method of determining water-soluble cations is likely to give erroneous results. The error may fall most heavily on Na and K, or on Mg and Ca.

If the purpose is to determine the base status of the exchange material of the soil as it occurs in the state of nature, the method used should at least be capable of showing that status. This can perhaps be most closely approximated by determining the soluble cations in the soil solution displaced at a moisture content corresponding to that of field conditions. However, it should be kept in mind that, as the moisture content of the soil changes through irrigation, rainfall or as a result of plant growth and evaporation, the soil solution itself changes both quantitatively and qualitatively. In consequence, the base status of the exchange material also changes. There is, therefore, no such thing as a true soil solution, nor an exact base status of the exchange material that is the same under different conditions. Both change as the water content of the soil changes. Nevertheless, water-soluble and exchangeable cations can in most cases be determined sufficiently accurately. In fact, high accuracy will probably serve no useful purpose.

In view of the uncertainties about the effects of carbonates, soluble silicates and CaSO_4 , Kelley and Brown (1934) proceeded as follows: Soluble Na and K were determined in 1 to 5 water extracts of the soil and again in extracts obtained by leaching a sample with N ammonium acetate. The water-soluble Na and K were subtracted from the amounts found in the ammonium acetate extracts, the difference being considered exchangeable Na and K. The NH_4 , adsorbed from ammonium acetate is also determined and the

amount found represents the exchange capacity. This quantity less the sum of exchangeable K and Na equals exchangeable Ca and Mg collectively.

Thus, in this method no attempt is made to determine exchangeable Ca and Mg separately. In view of the fact that the ratio of exchangeable Ca to exchangeable Mg found in soils of good tilth and of high productivity varies quite widely, it is believed that nothing will be gained with the vast majority of soils by determining Ca and Mg separately.

The important assumptions in this method are: (1) Water-soluble K and Na are adequately determined by analyzing 1 to 5 water extracts of the soil. (2) The soil contains no compounds of K and Na, other than water-soluble and exchangeable forms, which pass into the ammonium acetate solution. With many alkali soils assumption (1) is now known to be erroneous.

Reitemeier's Method. Reitemeier (1946) proposed a method by which exchangeable Ca, Mg and K can be calculated. This method involves the determination of soluble Ca, Mg, K and Na, at any moisture content desired, exchangeable Na by the ammonium acetate method, and cation-exchange capacity by the NH_4 -adsorption method. The formulas for calculating exchangeable Ca, Mg and K are theoretically applicable to any soil provided the factors used are dependable, but this method will probably be most useful with soils which contain substantial amounts of soluble salts. The calculation is based on the assumption that the replacing power of K ions is 5 times that of Na ions, and that the replacing power of Ca ions is 1.6 times that of Mg ions. As a matter of fact, these ratios are only very roughly approximate.

Representing exchangeable by X, the formula for calculating exchangeable K is:

$$KX = \frac{5(\text{Na}X)(\text{soluble } K^+)}{(\text{soluble } \text{Na}^+)}$$

Since NaX, soluble K^+ and soluble Na^+ are determined experimentally, KX can be readily calculated by this formula.

Base-exchange capacity is assumed by Reitemeier to be equal to the sum of exchangeable Ca, Mg, K and Na and this sum equals NH_4 adsorbed from ammonium acetate. Since adsorbed NH_4 is determined experimentally as well as exchangeable Na, and exchangeable K is calculated by the above formula, the sum of exchangeable

Ca and Mg represents the difference between exchange capacity (adsorbed NH_4) and the sum of exchangeable K and Na. Representing this difference by DX , exchangeable Mg is calculated by the following formula:

$$\text{MgX} = \frac{(DX)(\text{Mg}^{++})}{(\text{Mg}^{++})(1.6 \text{ Ca}^{++})}$$

CaX is then determined by difference.

This method of calculation need not be expected to give better than rough approximations, in view of the assumptions involved.

There appears to be no valid reason why exchangeable K cannot be determined experimentally as accurately as exchangeable Na. Therefore, the only essential difference between Reitemeier's and Kelley and Brown's methods is in the separation of exchangeable Ca from exchangeable Mg. With the possible exception of soils relatively high in dissolved Mg and low in dissolved Ca, there is probably no advantage to be gained by knowing what the ratio of exchangeable Ca to exchangeable Mg really is, granting that the ratio can be calculated accurately.

In view of the fact that water extracts of saline soils, however prepared, usually show greater amounts of soluble Na than are found in displaced soil solutions, and in some instances greater amounts of soluble Ca and other cations also, there is no valid reason why the soluble cations should not be determined by the displacement method. However, with heavy types of alkali soils it may be difficult to effect displacement of the soil solution. Probably the most practical procedure in such cases is to determine the soluble cations in extracts made at the lowest soil-water ratio possible. Certain workers have used a ratio of 1:1. In this connection, it is important to bear in mind that, if considerable sulfate is present in the sample, not all CaSO_4 present will be dissolved in the soil solution, nor will it all dissolve in 1 to 1 extracts. Consequently, special provision will need to be made for CaSO_4 dissolved by ammonium acetate. This is an additional reason for determining exchangeable Ca and Mg collectively rather than individually.

Base-Unsaturated Soils

When the exchangeable metallic cations have been replaced by H ions, the soil is said to be base-unsaturated. Varying degrees of base unsaturation are found. As the process of base removal de-

velops under natural conditions, the soil becomes acid. Base-saturated soils are most common in, though not confined to, regions of heavy rainfall.

The determination of the H ions, taken up in exchange for bases in the natural leaching process, presents a problem of special interest. Soils in general undoubtedly contain H that can be replaced as H ions only at relatively high pH. In fact the amount found may increase through a considerable range of pH. This has given rise to divergent views concerning (1) cation-exchange capacity, and (2) the content of, and methods for, the determination of exchangeable H ions.

Hissink's Method. Hissink (1924) proposed a method based on the idea that the base-unsaturated material is composed of weak insoluble acids. Since salts of weak acids hydrolyze, Hissink concluded that the exchange material can be base-saturated only at pH values well above neutrality. His method is as follows: Equal amounts of a given soil are placed in a series of test tubes to which different amounts of 0.1 N Ba(OH)₂ are added. Distilled water is then added to bring the content of each tube to 50 cc. After shaking occasionally for three days the soil is allowed to settle overnight, when aliquots are drawn off and titrated with 0.1 N HCl using phenolphthalein as indicator. The amounts of Ba(OH)₂ remaining in solution are plotted against the Ba(OH)₂ added, the former being shown on the vertical axis and the latter on the horizontal axis.

Owing to hydrolysis, the graph obtained will consist of a curved and a straight-line portion. The straight-line part of the graph is extrapolated to the horizontal axis, the point of intersection being considered the Ba equivalent of exchangeable H ions. Expressed as equivalents, the sum of exchangeable metallic cations (*S*) plus exchangeable H ions equals the total (*T*). Therefore, exchangeable H ions = (*T* - *S*). On the basis of his titration data, Hissink concluded that a soil at equilibrium with CaCO₃ may still contain substantial amounts of exchangeable H ions which in some cases may amount to as much as 50 per cent of the exchange capacity.

Mehlich's Method. Mehlich (1938, 1942, 1945) suggested the use of triethanolamine-BaCl₂ solution, 0.2 N with respect to Ba and of pH 8.2. As outlined in his last paper, a suitable amount of soil is leached with this solution followed by back-titration of the leachate. This gives the exchangeable H ions. The loss in Ba sustained by the solution is considered to be equal to cation-exchange capacity.

Mehlich (1945) obtained approximately the same results for several soils with the use of BaCl_2 -triethanolamine as with 0.2 *N* Ba-acetate.

Theories of Base Saturation. In line with the acidoid concept of Michaelis, as applied to soils by Bradfield (1923) and by Page (1926), the base-unsaturated material which occurs in soils largely as fine-grained particles of colloidal dimensions may, according to *Hissink*, be likened to insoluble weak acids. As with soluble polyvalent acids, like phosphoric, for example, some of the H ions on the surface of soil particles are assumed to dissociate more readily than others, and only at relatively high pH do all the H ions dissociate. In other words, the insoluble inorganic and organic acids are supposed to have two or more ionization constants. Hence, the soil can be fully base-saturated only at high pH, and accordingly greater amounts of base will be taken up from an alkaline than from a neutral solution.

According to *Mattson* (1931a, 1931b), OH ions of the soil basoids ionize as acids only at pH values above the isoelectric point and to an increasing degree as the alkalinity of the solution is increased, while the H ions of the acidoids dissociate at or near neutrality.

According to the *clay mineral concept*, as outlined in Chapter 2, the exchangeable cations, whether metallic or H ions, are those required to compensate for deficiencies in the positive charges of the lattice framework. Therefore, the cation-exchange capacity, at least of the montmorillonitic and hydrous mica clays, should be the same, regardless of what kind of cations make up this deficiency, provided all cations performing this function are replaceable at pH 7. For example, the H ions taken up by montmorillonite in exchange for metallic cations, whether by electrodialysis or by leaching with an acid, can be quantitatively replaced by leaching the sample with neutral acetate solution, and practically completely by leaching with neutral BaCl_2 or NH_4Cl , provided the leaching is sufficiently thorough. The amount of Ba or NH_4 ions thus taken up in exchange for H ions is practically the same as is found when the same sample was originally saturated with Ca or other metallic cations (see Table 25).

These data show that adsorbed H ions are replaceable by NH_4 ions at pH 7, and that the cation-exchange capacity at this pH is approximately the same whether the sample is saturated with Ca or H ions.

However, if an *alkaline solution* of equal concentration is used,

the results will not necessarily be the same. Usually when determined at pH above 7, the capacity is found to exceed that at neutrality. This is true to some extent of montmorillonite and may be quite marked with kaolinitic, halloysitic or organic soils. Why is this? In contrast to the explanations of Hissink, Bradfield, Page, and Mattson, the writer prefers the following:

On the edges of the montmorillonite lattice, OH ions are attracted by the terminal Al and Si ions and H ions are adsorbed by terminal O ions, thus forming additional OH ions also. More or less of the OH ions thus originating dissociate as acids at elevated pH and the resulting H ions are replaceable. However, since the area of terminal edges of montmorillonite crystals is small in proportion to the area of the flat surfaces, where the normal exchangeable cations,

Table 25. Replacement at pH 7 of Ca Ions and H Ions Adsorbed on Montmorillonite

	Replaced by NH_4^+ (m.e./100 gm)	Ignition Loss (%)
<i>Bentonite, Otay, California</i>		
Ca-saturated	110	21.83
H-saturated (electrodialyzed)	110	22.46
<i>Bentonite, Clay Spur, Wyoming</i>		
Ca-saturated	91	19.80
H-saturated (electrodialyzed)	93	18.12
<i>Bentonite, Goldfield, Nevada</i>		
Ca-saturated	104	21.51
H-saturated (electrodialyzed)	104	21.01

but no OH ions are located, the cation-exchange capacity of montmorillonite at elevated pH is not greatly in excess of that at neutrality.

On the other hand, kaolinite contains OH ions on one-half of the planar surfaces of lattice layers, and also OH ions on the terminal edges of the lattice, as with montmorillonite. Therefore, exchange capacity of kaolinite may be appreciably affected by the pH of the solution. With halloysite, OH ions at terminal position as well as in lattice positions likewise probably dissociate as acids at high pH. Moreover, the lathe shape of halloysite crystals and the internal structure of the mineral may have something to do with this question. In any case, Mehlick (1945) found that the amount of NH_4 adsorbed by halloysite from NH_4OH exceeded that taken up from neutral ammonium acetate. In addition to clay minerals, soils

also contain other substances, both organic and inorganic, which contain OH groups that may ionize as acids to some extent at high pH.

Thus, there are several substances that may influence the determination of exchangeable H ions at elevated pH. However, it appears probable that those H ions which serve to balance the charge on the framework of the lattice and which are replaceable by the cations of neutral acetate solutions, are the ones which influence soil properties most significantly. In the opinion of the writer, little will be gained by considering any others with the possible exceptions of those combined with organic substances.

Gedroiz (1924a) held that exchangeable H ions can be replaced by leaching with *N* BaCl₂, and can be determined by titrating the resulting solution.

Parker (1929) showed that the amount of Ba(OH)₂ required to raise the pH of an acid soil to 7.0, is approximately equivalent to the H ions that are replaced by leaching with neutral Ba-acetate solution. This indicates further that the exchange between H ions and Ba ions can be made complete at pH 7.

Cation-Exchange Capacity

The Use of Neutral Solutions. As commonly used in soil literature, cation-exchange capacity denotes the total cations that can be replaced from a given substance under a given set of conditions. Usually it is expressed as m.e./100 gm. It has been recognized for some time that the exchange capacity of a soil depends on the pH of the solution used in the determination. For this reason, and because of the facts set forth earlier in this chapter, neutral solutions should be used. In view of solubility and decomposition effects, Kelley and Brown (1924) recommended the determination of the cations absorbed from the solution rather than the amount of cations that are brought into solution from the soil. This quantity is now widely used in America as a measure of the cation-exchange capacity of acid, neutral and alkaline soils. Neutral *N* ammonium acetate is especially well adapted to this determination. With this salt the exchange capacity of inorganic soils can be determined reasonably accurately even when the soil contains soluble salts and CaCO₃. In fact the accuracy of the determination can be made about as great as that of total Ca, Al, Si, etc.; but high

accuracy depends on (1) thorough leaching of the sample and (2) accurate determination of NH_4 that has been taken up by exchange.

Since the NH_4 adsorbed from neutral ammonium acetate merely represents the amount of cations the soil is capable of holding in replaceable form at pH 7.0, and not the amount that could be held at some higher pH, the total cations brought into solution from strongly alkaline soils, exclusive of soluble salts and CaCO_3 , is not necessarily equivalent to the NH_4 adsorbed. To determine the exact base

Table 26. Effect of Leaching with $\text{Ca}(\text{OH})_2$ [Kelley and Brown, 1924]

	Brought into Solution with $N \text{ NH}_4\text{Cl}$ (m.e./100 gm)					
	Ca	Mg	K	Na	Total Bases	NH_4 Adsorbed
Yolo clay loam, untreated	21.8	6.1	1.3	1.2	30.4	27.3
Yolo clay loam, leached with $\text{Ca}(\text{OH})_2$	47.9	3.6	1.1	1.6	54.2	27.4
Clermont silt loam, untreated	3.4	0.9	0.2	0.5	5.4	6.1
Clermont silt loam, leached with $\text{Ca}(\text{OH})_2$	18.9	1.0	0.3	1.2	21.4	6.9
Rhonerville clay loam, untreated	2.6	2.0	—	0.3	4.9	8.6
Rhonerville clay loam, leached with $\text{Ca}(\text{OH})_2$	38.3	0.9	0.3	0.6	40.1	16.7
Hagerstown clay loam, untreated	1.0	0.9	0.2	0.8	2.9	6.8
Hagerstown clay loam, leached with $\text{Ca}(\text{OH})_2$	28.2	0.5	0.1	0.4	29.2	10.4
Melbourn clay loam, untreated	1.8	1.1	0.2	1.2	4.3	5.0
Melbourn clay loam, leached with $\text{Ca}(\text{OH})_2$	44.6	0.6	0.1	0.6	45.9	20.7
Greenville clay loam, untreated	3.0	1.0	0.1	0.9	5.0	3.2
Greenville clay loam, leached with $\text{Ca}(\text{OH})_2$	21.8	0.6	0	0.5	22.9	3.5

status of the solid constituents of strongly alkaline soils is probably impossible at present. The total amount is almost certainly in excess of the exchange capacity at pH 7.

This is well illustrated by data published by Kelley and Brown (1924). Several soils were first leached with $0.04 N \text{ Ca}(\text{OH})_2$ followed by leaching with distilled water. The samples were then leached with neutral $N \text{ NH}_4\text{Cl}$, as in the determination of exchangeable cations. The leachates were analyzed and the adsorbed NH_4 was determined. The results reported in Table 26 show that the

total bases brought into solution with NH_4Cl solution greatly exceeded the amounts of NH_4 adsorbed; whereas before leaching with $\text{Ca}(\text{OH})_2$ the two quantities were more nearly equal.

These data show that, in the case of three of the soils, the base-exchange capacity at pH 7, as measured by the NH_4 adsorbed, was not appreciably affected by treating the soil with $\text{Ca}(\text{OH})_2$. With the other samples the exchange capacity was increased to some extent. However, with all the samples the total bases brought into solution with NH_4Cl solution greatly exceeded the adsorbed NH_4 . Had the replacement been effected with an ammonium salt solution, the pH of which was as high as that of the soil after having been treated with $\text{Ca}(\text{OH})_2$, it is highly probable that much greater amounts of NH_4 would have been adsorbed. It follows, then, that the cation-exchange capacity at pH 7, as ordinarily determined by leaching with neutral ammonium acetate, is not necessarily a true measure of the base status of the soil at high pH. This point finds special application with certain kinds of alkali soils. While it is reasonably certain that in most alkali soils the content of exchangeable Na equals that brought into solution with ammonium acetate minus the amount dissolved in the soil moisture, the percentage Na saturation, as calculated, is likely to be erroneous. In some cases the percentage Na saturation thus calculated may even exceed 100. However, as was shown by Kelley (1937), data thus obtained afford a useful guide in following the chemical changes that are produced in strongly alkaline soil by chemical treatment.

Other kinds of salts can be used for the determination of cation-exchange capacity. With neutral or acid soils, the Ba adsorbed by thorough leaching with Ba-acetate is an accurate measure of cation-exchange capacity, and, if the soil contains considerable organic matter, the Ba adsorbed is probably a more accurate measure of capacity than the NH_4 adsorbed for the reasons already given. Bower and Truog (1940a) showed that $N \text{ MnCl}_2$, and $N \text{ KCl}$, gave about the same capacity as ammonium acetate. Among these salts, the choice is largely a matter of convenience.

Various investigators have determined cation-exchange capacity by titrating the electrolyzed or acid-leached material with standard alkali to pH 7 with $\text{Ba}(\text{OH})_2$, or to about pH 8.5 with NaOH . The results have not always been consistent. Recently Ross and Hendriks (1945) reported exchange capacities for a series of mont-

morillonites, determined by first leaching the sample with dilute HCl and then titrating to pH 8.3 with NaOH. The results were much lower with samples from certain bentonite deposits than are commonly obtained by the NH_4 -acetate method. An important difficulty encountered in the titration method is the indefiniteness of the end point. To reach a steady end point, several days may be required. By making the titration in a salt solution, KCl, for example, higher results are often obtained and less time is required to reach a constant pH.

A factor contributory to the unreliability of the titration method is the fact that the activity of exchangeable H ions apparently decreases as the percentage of base unsaturation decreases, reaching a low value as the H ions approach exhaustion. Then, too, the titrating solution used is usually quite dilute. When a dilute solution of NaOH is used, the complete replacement of all exchangeable H ions by Na ions is difficult for two reasons: (1) hydrolysis, (2) the low activity of the remaining adsorbed H ions. On the other hand, H ions, taken up in exchange for the ordinary exchangeable cations, can be readily replaced by leaching the sample with NH_4 -acetate. The fact that this is true indicates that the H ions taken up in exchange for metallic cations do not become "deeply buried in the silicate layer", as was suggested by Ross and Hendricks (1945, p. 39).

The Use of Acid Salts. Gedroiz (1916) concluded that exchange between Ca ions adsorbed on the soil and Al or Fe ions of normal solutions of their chlorides is approximately stoichiometric. On the other hand, Kelley and Brown (1926) concluded that when a soil is leached with a dilute solution of AlCl_3 , the exchange is effected chiefly by H ions formed by hydrolysis, rather than by Al ions. They found, however, that substantial amounts of Al were precipitated in the soil mass, presumably as $\text{Al}(\text{OH})_3$. Lutz (1938) found that the amount of Fe adsorbed from FeCl_3 by bentonite, expressed as Fe^{+++} , equaled about 2.5 times the cation-exchange capacity as determined with a neutral salt. Bower and Truog (1940b) found that the amount of certain elements adsorbed by montmorillonite and by Miami soil colloid from hydrolyzable salts of both divalent and trivalent bases, exceeded that adsorbed from salts of monovalent cations. They suggested that salts of divalent cations may ionize as divalent and monovalent cations, and that

salts of trivalent cations may ionize as trivalent, divalent and monovalent cations, all of which may take part in the exchange simultaneously. The amounts of Zn, Be, and Cu adsorbed from acetates exceeded the cation-exchange capacity as determined with NH_4 -acetate. Ferric and thorium chlorides, both of which are acid salts, gave exceptionally high values for exchange capacity.

In view of the foregoing discussion it can be asserted that considerable confidence that the cation-exchange capacity at pH 7 of inorganic soils is most accurately determined with an acetate solution, NH_4 -acetate or Ba-acetate. NH_4 -acetate, being a salt of a weak base and a weak acid, does not hydrolyze appreciably, and its solution is well-buffered. Consequently, the replacement of H ions by NH_4 ions does not greatly alter the pH of the solution. Moreover, the unused NH_4 -acetate of the solution is easily removed by volatilization and decomposition, and this facilitates the analysis of the residue.

With soils high in humus, the NH_4 -acetate method may give low results owing to the fact that NH_4 organic substances are somewhat soluble in NH_4 -acetate solution. Neutral Ba-acetate solution will probably give a more accurate measure of the exchange capacity with such soils. But, since base-unsaturated humus probably contains insoluble organic acids, it is not likely that these acids can be completely converted into salts at pH 7. It is probable, therefore, that a mildly alkaline solution should be used with base-unsaturated organic soils. Mehlich (1945) found that his BaCl_2 -triethanolamine method gave higher results with peat than the Ba-acetate method.

Electrodialysis. Various investigators have employed electrodialysis as a means of removing the exchangeable cations from soils. It is unnecessary to dwell at length on this method. It is tedious, often requiring many hours to effect complete removal of exchangeable Ca. Exchangeable Mg is still more difficult to determine by electrodialysis owing to the fact that $\text{Mg}(\text{OH})_2$ is precipitated on the walls of the anode chamber and on the anode itself. Furthermore, certain clay minerals seem to undergo slow decomposition when electrodialyzed. Samples containing no Mg that is exchangeable with other metallic cations, have been found to give up Mg when electrodialyzed for a prolonged period. More or less Si and Al also pass into solution. This indicates slow decomposition of the mineral.

Chapter 7

Cation Exchange in Relation to Soil Properties

Chemical Properties

Apart from CaCO_3 , the cation-exchange material is the most reactive part of the soil. Dilute acids, whatever their source, whether formed in the soil by biological processes, or introduced as constituents of rain water or commercial fertilizer, react chiefly with the exchange material. In this reaction H ions replace metallic cations. Thus in humid climates the cations of the soil solution are derived largely from the exchange material. When this material contains exchangeable H ions, it is able to react vigorously with CaCO_3 , with the evolution of CO_2 . Metallic Zn or Al placed in contact with moist acid clay is attacked with the evolution of hydrogen gas. As was shown by Graham (1940), certain primary minerals undergo chemical alteration when placed in contact with base-unsaturated clay. It is likely that tricalcium phosphate will be slowly converted into dicalcium or monocalcium phosphate by base-unsaturated clay. It follows, then, that the exchangeable cations are chemically active.

Exchangeable Na ions are readily replaced by H ions, even at the concentration in distilled water. This leads to the formation of NaOH. By reason of this fact Na clay is said to hydrolyze. Hence soil largely saturated with Na ions is commonly alkaline. Other metallic cations are also replaced by H ions.

Buffer Properties. Base-unsaturated clay tends to be acidic, but usually the pH is not as low as that of the solution which brought about the base-unsaturation. In other words, clay acts as a buffer towards acids. This is an important property of clay. But for this property, noncalcareous soils would rather quickly become acidic beyond the tolerance of plants, and further activity of important microorganisms would be seriously retarded.

As was pointed out in the preceding chapter, base-unsaturated clay behaves as if composed of weak acids. Exchangeable H ions dissociate to some extent, as would be expected of a weak acid, but

base-unsaturated clay is not, properly speaking, a weak polybasic acid. The titration curves fail to show definite breaks corresponding to two or more dissociation constants, as would be expected of a polybasic acid. Each exchangeable H ion appears to act more or less independently. Therefore, the exchange material acts as if it were monovalent, but this does not mean that clay contains truly monobasic acids. Rather each clay crystal contains many exchangeable cations.

Physical Properties

Most soils are granular when Ca-saturated; their tilth is favorable, save when the clay content is excessive. On the other hand, soils containing exchangeable Na ions tend to be dispersed and are relatively impermeable to water; their tilth is quite the opposite of that of the same soil when Ca-saturated.

Gedroiz (1924b) showed that the amount of the finest-sized particles, as shown by mechanical analysis, was greatly increased by saturating the exchange material with Na ions. He found that a substantial part of the silt and fine sand particles was broken down by Na saturation into ultra-fine particles. This was not the condition when the soil was Ca-saturated. Ca ions seem to bind the fine-sized particles into aggregates, whereas Na ions cause dispersion.

Peculiarities of Na-Saturated Soils. The very marked contrast between Ca-saturated and Na-saturated clay manifests itself in a large difference in settling volumes. A unit amount of Ca clay will settle from a suspension to a much smaller volume than the same amount of Na clay. The permeability of the former is usually much greater than that of the latter.

However, anomalous behavior is sometimes encountered. A soil, once dispersed in consequence of Na saturation, may not become granular by the mere replacement of Na ions by Ca ions. Some years ago the writer noted that on replacing Ca ions with Na ions by leaching with NaCl, a certain soil behaved peculiarly; if the Na-saturated soil was resaturated with Ca ions, without the intermediate removal of the occluded NaCl, little change in permeability of the soil took place. However, if the occluded NaCl was leached out, thereby bringing about pronounced dispersion of the particles before initiating resaturation with Ca ions, marked reduction in permea-

bility resulted. It seems that once a clay is highly dispersed, as by leaching with NaCl solution followed by leaching out the soluble electrolyte, the fine-sized particles do not always become reoriented immediately upon replacement of Na ions by Ca ions.

The results obtained by the writer with an irrigated sandy loam soil from Hemet, California, where the farmer had experienced considerable difficulty in wetting his soil to the desired depth, were in harmony with the foregoing statement. This soil contained considerable exchangeable Na. Upon leaching a sample with a saturated solution of CaSO_4 , the permeability was markedly increased; but this effect practically disappeared upon leaching out the soluble Ca salt. Despite the fact that approximately all exchangeable Na ions were replaced by Ca ions by leaching with CaSO_4 solution, the permeability to water again became low when soluble Ca ions were leached out.

Gardner (1945) also found that mere replacement of Na ions by Ca ions does not necessarily restore the granular condition that is essential to good tilth of soils and to rapid water penetration. Furthermore, Gardner found wide differences among different soils in this respect.

Suggested Explanations. A fully satisfactory explanation of the aforementioned results cannot now be given. It has been suggested, however, that under natural conditions the individual crystals of Ca-saturated montmorillonitic and hydrous mica clay tend to be oriented. Exchangeable Ca ions on the surface of the crystals possibly link adjacent particles together by sharing their charges between particles, thus building up aggregates. The Na ion, being monovalent, is unable to do this effectively. Consequently, the particles tend to fall apart upon replacing exchangeable Ca ions with Na ions, and this tendency is greatly accentuated by leaching out soluble electrolyte. When resaturated with Ca ions, the particles may not become reoriented at once.

This explanation is certainly inadequate to account for all the known facts. For example, Prof. A. O. Woodford called the writer's attention to the following striking phenomenon that was exhibited by Na-saturated montmorillonite. When air-dry, it appeared under high magnification to be in the form of relatively coarse flakes, each of which had fairly definite indexes of refraction. Upon allowing a drop of water slowly to flow across an air mount of the flakes, im-

mediately upon contact with water each flake suddenly and almost violently dispersed into particles of extreme smallness, many of which showed active Brownian movement. Upon contact with water, the Na-saturated clay acts as if a powerful repulsive force was set up between individual particles.

A possible explanation is the following: In the dry state the particles of Na clay lie close together owing to the fact that exchangeable Na ions are not hydrated. The particles then form aggregates of appreciable size by simple cohesion. Upon contact with water, exchangeable Na ions become hydrated and in consequence the primary particles disperse. However, in view of the violence of the dispersion, it seems probable that something more than mere hydration of exchangeable Na ions is involved. It is undoubtedly true that certain types of Na-saturated clay disperse to an extreme degree in water, and soils in general that contain more than a low percentage of Na saturation are less permeable to water than when Ca-saturated. Nevertheless, different soils are affected differently by a given percentage of Na saturation. When large numbers of soils are compared, the correlation between percentage of Na saturation and physical properties is often found to be poor. It appears that the dispersing effect of exchangeable Na ions varies from soil to soil. The specific kind of clay present is probably partly responsible for the lack of agreement, but, as yet, a fully satisfactory explanation remains to be given.

Neither do all badly dispersed Na soils remain relatively impermeable after being Ca-saturated. Experience has demonstrated that the highly dispersed and impermeable Na soil near Fresno, California, and also certain soils in other localities, rapidly become porous upon replacement of exchangeable Na ions by Ca ions. Why it is that different soils behave so differently in this regard is not known. This is another example of the incompleteness of present-day knowledge. Even widely accepted theories may need substantial revision in the future. There is great need for a better understanding of the forces that control the physical properties of soils.

When exchangeable metallic cations are replaced by H ions, as in the natural leaching of soils in humid climates, the clay material tends to become dispersed to some degree and to migrate downward along with percolating water. Also the H clay may slowly decom-

pose with the decomposition products accumulating in the subsoil. Thus dense subhorizons develop at the expense of the overlying soil. Since CaCO_3 tends to keep clay Ca-saturated, the downward migration of clay becomes pronounced only after CaCO_3 has been leached out.

Microbiological Activity

The soil may be impaired as a medium for the growth and activity of important microorganisms by the physical and chemical changes which accompany cation exchange. The removal of available Ca and the resulting low pH are especially important in this regard.

The relationship between exchangeable Ca ions and exchangeable H ions in soils has perhaps the most potent effect on microbiological activity. Soil microbiologists have shown that the azotobacter organisms are almost completely absent from certain Ca-depleted soils, and that when such soils are inoculated with viable cultures of azotobacter, the organisms soon lose viability. However, the addition of CaCO_3 overcomes this toxic condition. When the soil becomes excessively base-unsaturated, nitrification is retarded. The balance between the different groups of microorganisms may be greatly affected by base unsaturation.

Perhaps the most important biological effect of base-unsaturated soil is that shown by the legume bacteria. Until lime in some form has been applied, it has been found impossible to secure a stand of various legumes on vast areas in humid climates. In fact viable cultures of legume bacteria of various types may not retain their activity unless lime is applied.

Thus the microbiological effect of base unsaturation is of enormous practical importance. Knowledge on cation exchange has contributed greatly to the success of farming through its influence on crop rotation including the growth of legumes.

Soil Productivity and Plant Nutrition

Agronomists suspected, long before cation exchange was known, that the crop producing power of the soil was related to the absorptive power of the soil. As was pointed out in Chapter 1, attempts were made in the second half of the 19th century to correlate productivity with the absorptive (cation-exchange) power of the soil. The results were successful to a limited extent only. The failure to

find a general correlation is, of course, not surprising, since crop growth is not dependent on a single factor. At one time or another throughout the history of soil science, investigators have attempted, unsuccessfully in large part, to correlate crop yields with some one factor. At certain times the factor was nitrogen, phosphorus, potassium, or N P K supply; at other times the factor was lime, organic matter, or pH, and more recently plant nutrients in general including the so-called minor elements. However, the growth of plants depends not alone on plant nutrients. The water supply, state of aeration, temperature, light conditions and toxic constituents cannot be ignored. Therefore, crop productivity of soils in general can never be correlated with any one factor.

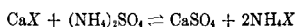
Nevertheless, the cation-exchange material contributes significantly to the growth of crops. Sir Daniel Hall, in the discussion following a symposium on base exchange held by the Faraday Society in 1924, stated: "A good soil is one that has got a large amount of exchangeable bases". The cations of the soil solution undoubtedly are readily utilized by growing plants, and, as has been pointed out, exchangeable metallic cations pass into the soil solution through exchange with H ions of biological origin. In the absence of CaCO_3 , the exchange material is the chief source from which the Ca ions of the soil solution are derived. It should not be inferred, however, that no other kind of substance contributes cations to the soil solution. Undoubtedly K and Mg ions, and possibly others to some extent, pass into solution from primary minerals through the weathering process. Neither should it be inferred that growing plants are dependent exclusively on the soil solution for metallic cations, as will be discussed later.

Effect of Fertilizers

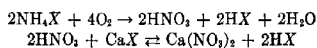
As is well-known, repeated applications of $(\text{NH}_4)_2\text{SO}_4$ to noncalcareous soil bring about marked reduction in exchangeable Ca with a corresponding increase in the acidity of the soil. Page and Williams (1925) found this to be the case in the permanent grass plots at Rothamsted. Merkle (1928) reported similar effects on the long-continued fertilizer plots of the Pennsylvania Experiment Station, and Aldrich *et al.* (1945) showed the same at the Citrus Experiment Station in California. Both Merkle and Aldrich found that the continued application of $(\text{NH}_4)_2\text{SO}_4$ may result in the accumulation of

abnormal amounts of exchangeable NH_4 in the soil. Apparently the acidity that results from the oxidation of NH_4 tends to reduce the action of nitrifying bacteria, so that the applied $(\text{NH}_4)_2\text{SO}_4$ accumulates as exchangeable NH_4 .

When $(\text{NH}_4)_2\text{SO}_4$ is applied to soil the following reactions take place:



where X refers to exchangeable. Upon nitrification:



Thus upon complete nitrification one molecule of $(\text{NH}_4)_2\text{SO}_4$ gives rise to 4 exchangeable H ions. However, Pierre (1928) showed that under cropping conditions the application of $(\text{NH}_4)_2\text{SO}_4$ yields only approximately 3 exchangeable H ions per molecule. This is accounted for by the fact that growing plants absorb considerably more equivalents of NO_3 ions than of Ca ions. A similar reaction takes place when any other NH_4 compound is applied.

Potassium salts react similarly except that K ions are not subject to oxidation like NH_4 ions. Where NaNO_3 is used as fertilizer, NO_3 ions are absorbed by growing plants, while the principal part of the Na ions replace metallic cations, or H^+ ions in the case of acid soils, with the resulting diminution in base unsaturation of the soil. Thus the use of NaNO_3 tends to reduce the acidity of the soil. Aldrich *et al.* (1945) showed that the application of NaNO_3 may result in substantial increase in the content of exchangeable Na ions in the soil and that this may cause reduced permeability of the soil. Similar reduction in permeability followed the application of $(\text{NH}_4)_2\text{SO}_4$.

Effect of Liming

The application of lime is one of the oldest practices of farmers. Liming dates back to the time of the Romans, perhaps earlier. For a long time, soil scientists explained the effects of lime on the assumption that lime increases the availability of K in the soil. Others attributed the beneficial effects to the improved physical effects that are produced. Later the effect was explained on the basis of the neutralization of organic acids. It is now known, however, that CaCO_3 may be beneficial regardless of the content of humus in the

soil. The development of knowledge on cation exchange has made possible a rational explanation of the effects of lime.

If the soil, whether organic or inorganic, contains exchangeable H ions, it reacts vigorously with CaCO_3 , whereby Ca ions replace H ions. By this means the acid condition is neutralized. This is the chief chemical effect of lime, and the chemical reaction is often accompanied by pronounced physical effects also. As the H ions are replaced by Ca ions the particles tend to coalesce into larger aggregates.

Thus, it is the cation-exchange material that is chiefly affected by liming and generally speaking it is only base-unsaturated soils that respond to lime. Since these soils rarely contain more than a very small amount of exchangeable K ions, the effects of lime on the availability of K is not the main reason for the beneficial effects. Experience has demonstrated that the amount of lime applied should usually fall somewhat short of that required to replace the last trace of exchangeable H ions. A full explanation of this fact cannot now be given. Perhaps, it is connected with the effects of pH on the solubility and availability of other ions, certain minor elements in particular.

In any case, the primary reasons for applying CaCO_3 is to increase the content of exchangeable Ca ions in the soil. Since base-unsaturated soils are usually deficient in exchangeable Ca ions, the effect of CaCO_3 application is commonly most pronounced with these soils. The low pH of acid soils is indicative of Ca deficiency and it is largely because CaCO_3 overcomes this deficiency, rather than because of the effects on pH, that applications of CaCO_3 or of other alkaline compounds of Ca, are agriculturally beneficial. During recent years enormous amounts of CaCO_3 have been profitably applied in humid climates. Frequently, it has been found impossible to secure good growth of legumes without applying lime.

Potassium Fixation

Owing to cation exchange, K ions, applied as soluble salts, are readily adsorbed by the soil. Not infrequently a high percentage of the applied K is adsorbed within a few inches of the places where the fertilizer is incorporated in the soil. Therefore, K is not subject to extensive loss by leaching except with extremely sandy soil. Until recently it was believed that the adsorption of K ions was completely reversible.

Dyer (1894) reported that after 38 annual applications of K fertilizer, the soil of the Hoos Field at Rothamsted showed an increase in K soluble in strong HCl approximately equal to the amount that had been applied after allowing for the K removed in the crops grown. Frear and Erb (1918) obtained similar results on the soil of the Pennsylvania Experiment Station after 18 applications of KCl at the rate of 200 pounds per acre. However, in neither the Rothamsted nor the Pennsylvania soil was more than $\frac{1}{3}$ of the residual K soluble in dilute acids, 1 per cent citric acid in the case of the Rothamsted soil and 0.2 N HCl with the Pennsylvania soil. These results indicate that only a part of the residual K is readily exchangeable for H ions.

Volk (1934) showed that under the conditions used in his experiments many, but not all, soil types have the power to fix K ions in nonreplaceable form. From special studies he concluded that muscovite has been formed in the Hagerstown soil of the Pennsylvania Experiment Station as a result of KCl application over a period of years. In view of the fact that muscovite is a high-temperature mineral, there is reasonable ground for doubt about the formation of muscovite *de nova* under soil conditions. Moreover, it remains to be shown that the original muscovite content of the two plots studied by Volk was the same. As was shown by Frear and Erb (1918), the total K content of these plots differed substantially.

Truog and Jones (1938), Page and Bayer (1939), and Martin *et al.* (1945) found that the fixation of K ions by soils and by bentonite was associated with a corresponding reduction in cation-exchange capacity. Page and Bayer found that the fixation of cations by both bentonite and Miami soil colloid is not confined to K ions, but that a considerable number of other kinds of cations are also fixed.

Certain workers have suggested that the fixation of K ions by montmorillonite may be due to the binding together of adjacent lattice layers by K ions, which thus entraps K ions. The following consideration seems to cast doubt on this explanation. Since the fixation of K ions has been reported as taking place when the material is only partially K-saturated, in fact but slightly so, if the fixation takes place as a result of entrapment, then other associated exchangeable cations should also be entrapped, and hence the reduction in exchange capacity should be several-fold as great as the amount of K fixed. This, however, appears not to be the case.

While the fixation of K ions appears to be well established both in the laboratory and under field condition, the fact that a reduction in cation-exchange capacity roughly equivalent to the K fixed may take place in the laboratory, is not well supported by field evidence. For example, Page and Williams (1925) showed that the exchange capacity of the Broadbalk plots at Rothamsted after 82 annual applications of K fertilizers was approximately the same as that of plots not fertilized with K. The theoretical aspects of K fixation have not been well elucidated. No theory thus far proposed explains all the facts of K fixation.

Effect of Cropping

It is well-established that under natural conditions in humid climates exchangeable Ca and other cations are gradually replaced by H ions and are leached out as bicarbonates. Under cropping conditions this process is augmented by the absorption of metallic cations by the crops, the greater part of which is taken away from the soil where grown in the harvested crops. The result is that under cropping conditions the soil tends to become depleted of exchangeable metallic cations. This is not true of grassland soils under natural conditions. Here the annual growth falls down and decays, leaving the cations on or near the surface or beneath the surface where plant roots decay. The leaching action of rains tends to redistribute the cations to some depth below the surface.

The corn belt soils of Illinois and other states gradually lost exchangeable Ca ions when first brought under cultivation. The result was that the soil, although approximately neutral originally, became acidic. This process of cation depletion applies to all cultivated soils and will become serious in the course of time unless artificial applications are made. Cropping is indeed an effective way of producing deficiency in metallic cations of the soil. It is largely because of this fact, together with the loss of N and P, that artificial manuring is indispensable in good soil management.

Martin (1929) showed that annual cropping to barley for nine years, without the application of any kind of fertilizer, brought about a material reduction in the exchangeable K of every one of more than a dozen soil types. Fortunately this loss of K and of other elements can be compensated for by the application to the soil of the right kind of fertilizer.

The effects of cropping on exchangeable Mg may not be so serious

as with exchangeable Ca. Gedroiz (1931) found that the growth of oats, mustard and buckwheat on a chernozem soil was unimpaired by artificial replacement of practically all exchangeable Mg ions by Ca or H ions. This soil contained relatively much nonexchangeable Mg. Since Mg is an essential element, the plants grown must have absorbed Mg from some source. On the other hand, Mg-deficient soils are fairly common along the southern Atlantic Coast of America. Cropping has probably contributed to this deficiency.

In any case it is certain that cropping, without the use of manures or fertilizers is a potent means of reducing the content of exchangeable Ca and K in the soil.

Contact Effects

Jenny and Overstreet (1939) showed that certain exchangeable cations can be absorbed by plant roots, and possibly without the cation passing through an intermediate solution stage. This result has been further confirmed by Jenny, *et al.* (1939). The opposite is also probably true, namely, the exchange material may absorb metallic cations from plant roots. For example, if the exchange material is largely saturated with a kind of cation that readily exchanges with Ca or K ions, such as Na or Mg ions, plants growing in such soil may actually lose more or less Ca and K to the exchange material [see Jenny and Overstreet (1939); Jenny, *et al.* (1939); Albrecht and McCalla (1938)]. By this means Ca and K ions, originating in the mother seed, may pass out of the plant and be taken up by the exchange material.

The results of an experiment by the writer about 20 years ago bear on this point. A productive porous sandy soil free from CaCO_3 was artificially saturated with Na ions by prolonged leaching with a solution of NaCl. After removing soluble electrolyte, barley seeds were planted in this material. The moisture content at the time of planting was approximately that of good tilth. When the seeds had germinated, the seedlings were allowed to grow for a few weeks in a moist chamber, but without replenishing the moisture content of the soil.

Na-saturated soil is known to be an unfavorable medium for plant growth. The toxicity has been attributed to excessive alkalinity and to unfavorable physical conditions. The pH of this Na-saturated soil was not more than 7.8, which is well within the range

of tolerance of barley plants. The soil, being quite sandy, was loosely packed in the containers; hence it is probable that the oxygen supply was not a limiting factor. Nevertheless, this soil proved to be highly toxic to barley. Commenting on this experiment Kelley (1927, p. 4) stated: "The roots that were formed never became more than a few millimeters in length and they were coarse and stubby. The appearance of the roots suggested a highly toxic condition. Investigation showed that the *soil solution* was entirely *nontoxic*. The toxic factor was, therefore, not present in the liquid phase".

The suggestion made in 1927, now greatly strengthened by the work of Jenny and Overstreet, was that Ca ions, derived from the seed by the barley seedlings, were exchanged for Na ions of the soil, the result of which was the seedlings lost some at least of this Ca. Thus the seedlings were able neither to obtain Ca from the soil, nor to retain that inherited from the seed. The consequence was the young plants died within a few weeks. In the light of the work of Jenny and Overstreet, it is likely that K ions also passed out of the roots in exchange for Na ions. Thus by exchange with the soil, the seedlings became severely deficient in both Ca and K. The fact that alkali soils which are high in exchangeable Na are often found to be highly toxic to germinating seedlings is probably due in considerable part to the type of reaction just discussed.

Chapter 8

Identification and Estimation of the Clay Minerals

The investigations of Hendricks and Fry (1930) and of Kelley, Dore and Brown (1931), showing that the inorganic colloidal material of soils is crystalline, have led to the development of methods for the identification of the cation-exchange materials, that is, the clay minerals of the soil. It is now well established that two or more kinds of clay minerals are present in the vast majority of soils. In certain soil types one type of clay may greatly predominate over other types, but rarely has it been found that a single type of clay is present. The variations in the relative amounts of different kinds of clay in different soils are very wide.

The methods of identification now available include x-ray analysis, dehydration, differential thermal analysis, optical, electron microscopic, chemical analysis and cation-exchange capacity determination. Unless a given kind of clay comprises a considerable percentage of the total, none of these methods gives absolute identification or permits accurate determination of the amounts present, but by combining two or more methods, it is usually possible to determine what type of clay predominates, and in some cases, at least, to make an approximate estimate of the relative amounts of the different types that are present.

X-ray Analysis

Although x-ray diffraction patterns show several lines that are common to all the clays, the (001) spacings of each clay are distinctive. Advantage may be taken of this fact in the identification of the clays.

Montmorillonite. Hofmann, Endell, and Wilm (1933) discovered that the (001) spacing of montmorillonite varies with the water content of the sample. As shown in Table 27, when the sample is water-saturated, this spacing was found to be approximately 20 Å, and as water was expelled, this spacing gradually

contracted, reaching a minimum of 9.6 or 10 Å. These results have been verified by other investigations. The expansion of the (001) spacing is commonly referred to as inner crystalline swelling. The other spacings of montmorillonite are not affected by the water content, and except for diminished intensity they remain unchanged up to about 500°.

Hendricks *et al.* (1940) showed that both water content and kind of exchangeable cation influence the (001) spacing of montmorillonite. Samples of Ca- or Mg-saturated montmorillonite, dried in vacuum over P_2O_5 and then exposed to an atmosphere of 50 per cent relative humidity, were found to absorb 22 per cent H_2O , which is close to the total water content (ignition loss) of the air-dry material. At this moisture content the (001) spacing was approximately 15 Å. On the other hand, K-saturated montmorillonite

Table 27. Contraction of Montmorillonite upon Drying [Hofmann *et al.*, 1933]

	From France		From American Bentonite A		From American Bentonite B	
	H_2O (%)	(001) (Å)	H_2O (%)	(001) (Å)	H_2O (%)	(001) (Å)
H_2O -saturated	>30.00	19.6	>30.0	18.0	>25.0	22.0
Air-dry	22.75	15.2	24.5	15.7	18.0	15.2
Heated to 100°	8.75	11.2	7.5	11.5	6.0	11.0
Heated to 200°	7.00	9.9	5.7	10.0	4.5	10.5
Heated to 350°	6.80	9.8	4.5	9.8	4.0	10.0
Heated to 550°	4.60	9.6	2.8	9.6	—	—

absorbed only 10.0 per cent H_2O from the same atmosphere and the (001) spacing was 11.9 Å. Na-saturated montmorillonite gave (001) reflection too diffuse for accurate measurement.

Contrary to common belief, Hendricks *et al.* found that throughout the range of relative humidities from 5 to 90 per cent Na-saturated montmorillonite adsorbed less water than Ca- and Mg-saturated forms. These results were explained on the basis of differences in the hydration of the exchangeable cations. The total water adsorbed by Ca- and Mg-saturated montmorillonite represents the sum of water of hydration of exchangeable cations plus that adsorbed by the surfaces between exchangeable cations, whereas the total adsorbed by Na-, K- and H-saturated montmorillonite is exclusively water of hydration of surfaces. This latter water is attracted by relatively weak van der Waals forces and is expelled at a lower temperature than water of hydration of exchangeable cations.

Jackson and Hellman (1941) found, in agreement with Hendricks *et al.*, that Ca-saturated montmorillonite gives sharp x-ray lines and especially so if the sample is dried from benzene. Aldrich, Hellman and Jackson (1944) found that uniform hydration of the sample is a further aid in the identification of montmorillonite. They recommended first Ca saturation and then shaking with a mixture of benzene and ethanol containing a definite amount of water in order to effect uniform hydration of all parts of the sample.

Thus it appears that Ca saturation and careful control of the moisture content of the sample will facilitate the identification of montmorillonite. K-saturated material should be avoided; otherwise it may be difficult to distinguish between montmorillonite and hydrous mica.

The writer and colleagues and various other investigators have encountered no difficulty in the x-ray identification of montmorillonitic clay by simply drying the Ca-saturated form at room temperature. There is, in fact, a great deal of evidence that this can be done. Since Ca ions and Mg ions constitute a high percentage of the total exchangeable cation in normal soils, it is doubtful whether artificial Ca saturation is even necessary for identification except perhaps with extremely acid soils or alkali soils.

MacEwan (1946) showed that by treating montmorillonite with glycerol a complex is formed which shows much sharper x-ray lines than ordinary montmorillonite. Furthermore, the first order, basal reflection (001), with this material is 17.7 Å, whereas, with ordinary Ca-saturated montmorillonite dried at room temperature, this spacing is 15 to 16 Å. It appears that glycerol takes up a position between lattice layers corresponding to that occupied by H₂O in ordinary montmorillonite. A noteworthy feature of the montmorillonite-glycerol material is that essentially the same sharpness and position of the x-ray lines are obtained whether the exchangeable cation is monovalent (Na, K, NH₄) or divalent (Ca, Mg). MacEwan reports that as little as one per cent montmorillonite can be easily identified by this method. Therefore, it appears to be exceptionally valuable for the identification of montmorillonite in soils.

Hydrous Mica. It has been held for sometime that the widest spacing of hydrous mica is approximately 10 Å, and that this spacing remains constant over a considerable range of temperature, that is the crystal of hydrous mica does not swell by taking up water

between lattice layers. However, Jackson and Hellman (1941) and Aldrich *et al.* (1944) claim that when fully hydrated certain samples of alleged hydrous mica gave an x-ray line at 12 to 13 Å.

One of the most serious difficulties in the identification and quantitative determination of hydrous mica lies in two facts: (1) Hydrous mica is the name applied to a group of substances which in many localities at least are apparently formed by varying degree of alteration of mica (perhaps biotite chiefly). As yet we do not know definitely just what this alteration involves. Undoubtedly it involves the replacement of more or less K ions by H ions, but it is not certain that more fundamental changes do not take place also; for example, the oxidation of ferrous to ferric iron or even the alteration of both the tetrahedral and the octahedral layers of the lattice. It is even possible that mica may, under conditions not yet fully understood, alter to a substance closely resembling montmorillonite, at least to a substance with a definitely expandable type of lattice. In other words there may not be a sharp dividing line between hydrous mica and montmorillonitic clay. (2) According to Hendricks and Alexander (1939) and Ross and Hendricks (1945) layers of hydrous mica and of montmorillonite may be intergrown in the same crystal. Where this is the case, complete separation will be impossible.

In any case, various workers have found a clay substance in soils which gave a 10 Å spacing that remained constant over a considerable range of water content.

Hellman, Aldrich and Jackson (1942) were unable to detect the wide spacing of hydrous mica in mixtures of montmorillonite containing as much as 40 per cent hydrous mica. In such mixtures the very presence of hydrous mica could be judged only by the weakening of the corresponding montmorillonite lines. Since soil colloids may contain admixtures of various substances including clay minerals and nonclay substances, some of the latter even being amorphous, the results of Hellman *et al.* suggest that the x-ray method is poorly adapted to the identification of hydrous mica. As was pointed out in the second paragraph of this chapter, no single method is adequate for the quantitative determination of the individual clay minerals in soils.

Kaolinite. The widest spacing of kaolinite is approximately 7.2 Å, which spacing is apparently not influenced either by the water

content of the sample or by the nature of the exchangeable cations. The minimum amount of kaolinite that can be determined by x-ray method is probably not less than 5 per cent of the sample and may possibly be even more than 5 per cent in heterogeneous material like soil colloids.

From the foregoing it is apparent that it is difficult to determine by x-ray method the several clays when present in low percentages. Fortunately other methods can be used to supplement x-ray analysis, but, as will be seen, there appears to be a minimum below which the quantitative determination of the several clays is quite uncertain.

As a qualitative basis of judgment, Kelley *et al.* (1939a, 1939b) used the following method: Ca-saturated soil colloids, freed from organic matter by oxidation with H_2O_2 , were dried at room temperature, then exposed in thin layers at room temperature to an atmosphere of approximately 50 per cent relative humidity for several weeks. After x-raying, the samples were heated to constant weight at 500° and x-rayed again. If the unheated sample showed the 15 Å line which shifted to approximately 10 Å upon heating, it was concluded that montmorillonitic clay was present. A 10 Å line in the diffraction pattern for the unheated sample indicated hydrous mica and a 7.2 Å line, which either disappeared altogether or became very weak upon heating to 500° , was taken to be an indication of kaolinite. Kelley *et al.* made no attempt to estimate the relative amounts of the different clays, nor to determine the minimum amounts that can be detected by this method. However, the relative strengths of the several (001) lines give a rough indication as to the amounts of the different clay types present in the sample. For example, it was concluded that the Yolo soil colloid of California is predominantly montmorillonitic, that the clay of the San Joaquin and Hanford soils of California is predominantly hydrous mica, although most of the samples also contained considerable kaolinite, and that the Sierra soil colloid from California and a sample of Cecil from Alabama are largely kaolinitic. Recent studies by Coleman and Jackson (1945) have confirmed the above conclusion insofar as the Cecil colloid is concerned.

It should be pointed out in this connection that the separation of the sample into two or more particle-size ranges may be a material aid in the identification of the clay minerals. The previous

work of the writer dealt with particles less than 1μ . As will be shown later, montmorillonite is likely to be present chiefly as particles of extreme smallness, 0.3μ or less, whereas the particles of kaolinite and possibly of hydrous mica are commonly larger.

Dehydration

Kaolinite. When hydrous minerals are heated, the lattice OH ions pass off as H_2O at temperatures characteristic of each mineral. Adsorbed water usually volatilizes at relatively low temperature. The dehydration curve of kaolinite is highly distinctive. This mineral adsorbs relatively little water and its OH ions pass off as H_2O at a fairly definite temperature (about 500°). Since kaolinite contains more than twice as much water of constitution per unit weight as either montmorillonite or hydrous mica, the dehydration curve of kaolinite is readily distinguished from that of the other clay types.

Montmorillonite. This mineral also gives a fairly definite dehydration curve. Its most pronounced characteristic is shown in the magnitude of water loss at temperatures below 150° . This is due to adsorbed water which is held chiefly between lattice layers—the so-called swelling water that is associated with the expansion of the (001) spacings. The lattice OH ions pass off as H_2O at a higher temperature and give rise to a wave-like dehydration curve. For reasons not well understood, the lattice OH ions of montmorillonite pass off as H_2O over a considerable range of temperature, and much more so than the OH ions of kaolinite. The spread in the temperature over which lattice OH ions of montmorillonite volatilize as H_2O , and the fact that samples from different sources differ in this regard, indicate that OH ions are held in lattice positions of montmorillonite by attractive forces of varying strengths.

Ross and Hendricks (1945) reported that the volatilization loss above 300° of montmorillonite from different sources ranges from about five per cent to more than eight per cent. When it is recalled that the formula proposed by Ross and Hendricks provides for lattice OH ions equivalent to 4.91 per cent H_2O , one or the other of two alternatives must follow: (1) The proposed formula does not correctly represent montmorillonite from all sources, or (2) some of the samples contained hydrous impurities of some sort, interleaved or admixed. Those samples which sustained water losses

of about 5 per cent at temperature above 300°, Ross and Hendricks called normal montmorillonite. Presumably they consider abnormal those with more than 5 per cent H₂O, but the specific nature of the abnormality is not made clear in their paper.

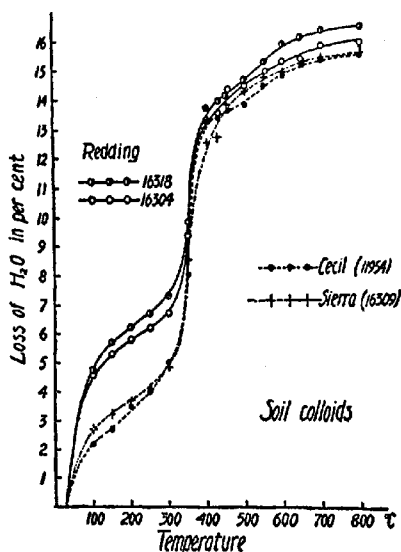


FIGURE 3. Dehydration curves for soil colloids
 Redding 16318—Butte County, California
 Redding 16304—San Diego County, California
 Cecil 11954—Cecil, Alabama
 Sierra 16309—El Dorado County, California
 [Reproduced from Kelley, Jenny and Brown, 1936]

Hydrous Mica. Hydrous mica gives a dehydration curve similar in shape to that of montmorillonite but with considerably less water loss at low temperatures. In this particular the curve for hydrous mica is intermediate between the montmorillonite and kaolinite curves. Figures 3 and 4 show typical dehydration curves for kaolinitic soil colloids.

The ordinary dehydration curves of montmorillonitic soil colloids are not especially distinctive. When heated montmorillonitic clay

loses relatively much water at comparatively low temperature (50 to 200°). Accordingly, the dehydration curve rises steeply in this

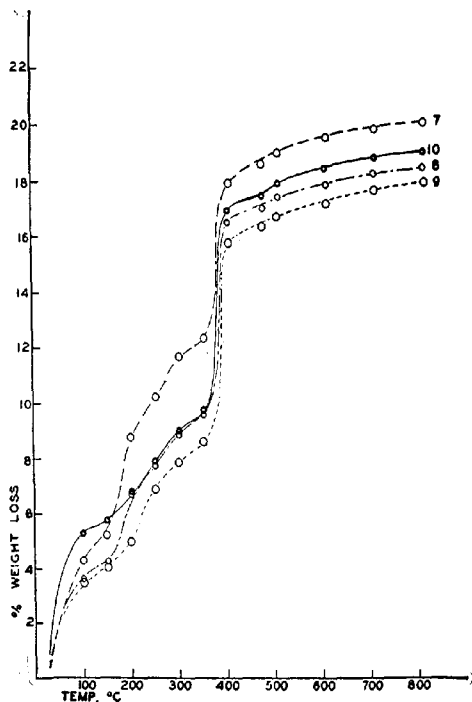


FIGURE 4. Dehydration curves for Aiken soil colloids from Paradise Ridge, California

7—0" to 12"
 8—15" to 25"
 9—40" to 48"
 10—60" to 75"

temperature range. Hydrous mica also contains considerable low-temperature water, but by no means as much as montmorillonite.

Differential Thermal Analysis

The volatilization of water, whether adsorbed or derived from lattice OH ions, is accompanied by the absorption of energy. This

is reflected by a lag in the temperature of the sample relative to that of an anhydrous reference material, like Al_2O_3 , that is being

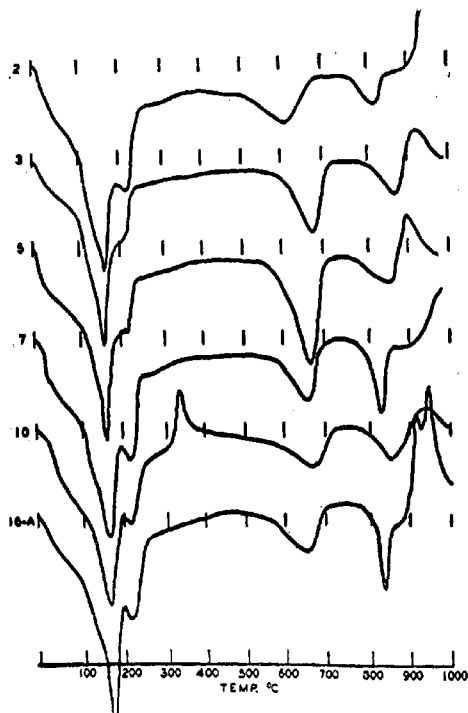


FIGURE 5. Differential thermal curves for montmorillonite from bentonites

2—Otay, California

3—Clay Spur, Wyoming

5—Rosedale, Alberta, Canada

7—Goldfield, Nevada

10—Death Valley Junction, California

16-A—Newberry, California

[Reproduced from Page, 1948]

heated at the same rate. On the other hand, energy is set free in the oxidation of carbonaceous material and also as a result of certain molecular rearrangements. The differential thermal method shows the temperatures at which these effects take place. An endothermic

dip in the curve indicates the loss of water, and exothermic reactions are reflected by rises in the temperature above that of the reference material. The temperatures at which these reactions take place are highly characteristic for kaolinite and fairly so for montmorillonite. Unfortunately, the thermal curve for hydrous mica is not always clearly distinguishable from that of montmorillonitic soil

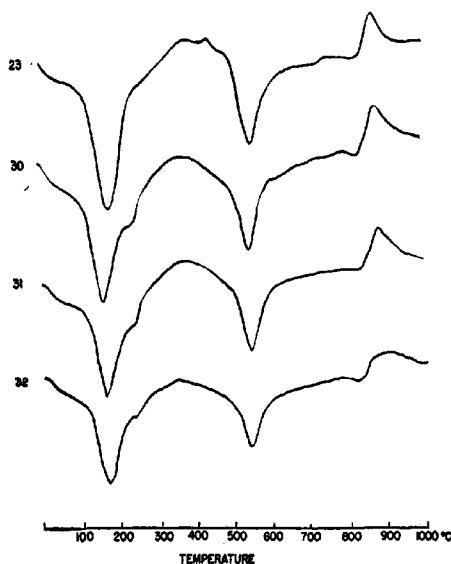


FIGURE 6. Differential thermal curves for Stockton clay adobe soil colloids from Chico, California

23—6" to 13"

30—0" to 28"

31—28" to 40"

32—40" to 70"

clay. Usually, however, the endothermic effect at low temperature is less pronounced with hydrous mica.

Figure 5 shows differential thermal curves for a series of montmorillonite samples from bentonite, and Figure 6, curves for montmorillonitic clay from the Stockton soil series. Figure 7 shows the curves for the kaolinitic clay of an Aiken soil profile.

It will be noted that the Stockton soil colloids show a marked

endothermic effect at about 150° , as do the montmorillonite samples from bentonite. They also show an exothermic reaction between 800° and 900° , which is characteristic of many bentonites. The

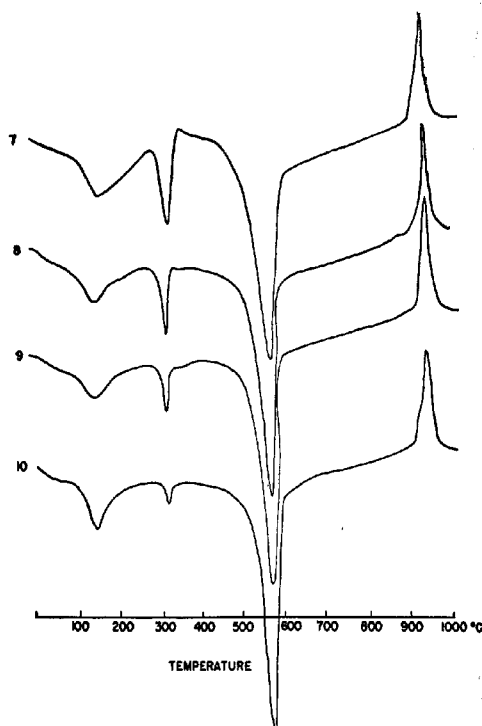


FIGURE 7. Differential thermal curves for Aiken soil colloids from Paradise Ridge, California

7—0" to 12"
8—15" to 25"
9—40" to 48"
10—60" to 75"

pronounced endothermic effect at about 550° , shown in Figure 6, indicates the presence of kaolinite. Thus the Stockton soil colloid appears to be composed of a mixture of montmorillonitic and kaolinitic clay.

In contrast to the Stockton soil, the Aiken soil colloid (Figure 7) is very largely kaolinitic clay. The endothermic dip at about 300° indicates small amounts of some hydrated oxide of iron, perhaps limonite, but the pronounced endothermic effect at about 550° and the sharp exothermic reaction at about 900° strongly indicate kaolinitic clay. These curves are quite consistent with the x-ray evidence on the same samples.

Although the thermal curves of montmorillonite from bentonite can usually be readily distinguished from the thermal curves of hydrous mica, it is not certain that a clear distinction between these minerals in the case of soil colloids can always be made by thermal methods. On the other hand, fairly reliable identification of kaolinitic clay can be made by this method, provided the amount present exceeds 5 to 10 per cent of the sample.

The samples used for thermal study should be as free as possible from organic matter and carbonates. Otherwise it is likely to be still more difficult to interpret the curves owing to the fact that the exothermic effect of oxidizing organic matter may counteract the endothermic effect of water volatilization.

Optical Methods

The indexes of refraction of montmorillonite and kaolinite are fairly distinctive. The alpha index of montmorillonite from bentonite commonly varies from about 1.490 to 1.530 with a birefringence of from 0.020 to 0.030, while the corresponding values for pure kaolinite are approximately 1.560 and 0.005. However, the refractive index of montmorillonitic soil clays is commonly greater than that of bentonitic clay, and the same is true as between pure kaolinite and kaolinitic clay from soils. The refractive index of the latter is commonly 1.600 or more. It is probable that the iron content of soil clays tends to increase their refractive indexes.

Perhaps the most useful optical property of soil clays is their birefringence. Kelley *et al.* (1939a) found that the birefringence of the colloids from a Susquehanna soil profile increased with depth roughly proportional to the content of montmorillonite as determined by x-ray and dehydration methods.

Since considerable experience in the use of the petrographic microscope is required for the accurate measurement of the optical properties of fine-grained materials, this method is not well suited for general use.

The Electron Microscope

The electron microscope has not been used extensively with soil colloids. Its usefulness will perhaps be greatest as an aid in distinguishing between kaolinite and halloysite. The well-developed hexagonal plates of kaolinite are clearly recognizable under the electron microscope, while halloysite shows needle-like or lathe-shaped crystals. Among the few kaolinitic soil colloids that have been studied with the electron microscope, it appears that kaolinite is much more abundant than halloysite. Montmorillonite and hydrous mica are difficult to identify in soil colloids by this method, owing to the irregular boundaries of individual crystals.

Chemical Analysis and Cation-Exchange Capacity

Generally speaking, chemical analysis has not thrown much light on the clay mineral content of soils. This is largely due to two facts: (1) The difficulty of obtaining a sample that is composed exclusively of a single clay mineral. Usually uncombined oxides and hydroxides and colloidal silica are also constituents. (2) The three-layer clay minerals, as suggested in previous chapters, represent an extensive and intricate isomorphous series. For these reasons the ratios of elements vary considerably in the purest samples obtainable. However, the molecular ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and of $\text{SiO}_2/\text{R}_2\text{O}_3$ of soil colloids, found to be kaolinitic by other methods, are commonly considerably less than the corresponding ratios of montmorillonitic soil colloids. The $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of pure kaolinite is 2.00, whereas the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of montmorillonite varies from about 3 to only slightly less than 4.

Certain workers have used the K_2O content of soil colloids as a basis of calculating the content of hydrous mica. This calculation can hardly give more than a rough approximation, since the K content of hydrous mica from different sources has been found to vary considerably.

If the sample is composed largely of one type of clay mineral, the exchange capacity will indicate what that mineral is, but with uncertain mixtures, the exchange capacity is difficult to interpret. The determination should be made on material representing a series of particle-size ranges. By this means it is possible to make an approximate estimate of the amount of montmorillonitic clay present. This type of clay tends to be present as extremely small particles.

For this reason the exchange capacity of soil particles less than about 0.3μ is likely to be substantially greater than that of larger particles. The exchange capacity of montmorillonite from bentonite usually ranges from about 90 to 110 m.e./100 gm expressed on the air-dry weight.

It is usually difficult to interpret exchange-capacity data on samples containing mixtures of clay minerals. The exchange capacity of pure kaolinite is commonly not more than 10 to 15 m.e./100 gm, whereas that of hydrous mica appears to vary from about 30 to 40 m.e./100 gm.

Since soil colloids are rarely composed of a single type of clay but commonly contain two or more types of clay admixed with other substances from which complete separation is difficult, the exchange capacity of highly montmorillonitic soil colloids has rarely been found to exceed 75 m.e./100 gm.

The Clay Minerals of Different Soils

Until a few years ago soil scientists made no attempt to separate the different kinds of clay in a given soil. If the x-ray or thermal evidence indicated the presence of montmorillonitic clay, the conclusion was that the soil was montmorillonitic. If the evidence was strong for kaolinite, the soil was put down as a kaolinitic soil. However, about ten years ago it began to be recognized that the problem was not so simple. Evidence that mixtures of different types of clay are common in soils has now become convincing.

Estimates of the clay minerals in the soils from various parts of the United States have been made by Alexander *et al.* (1939), Kelley *et al.* (1939a, 1939b), Russell and Haddock (1940), and by Coleman and Jackson (1945). Favejee (1939) made similar estimates on the soils of Holland. Jacob *et al.* (1935) indicated the kind of clay that predominates in soils from various parts of the world, and Nagelschmidt *et al.* (1940) estimated the clay minerals of a black cotton soil and a red earth soil from India. Similar estimates were made on certain soils of the Netherland East Indies by Hardon and Favejee (1939).

The results of these investigators, while differing in detail, agree remarkably well in showing that, with very few exceptions, two or more types of clay are found in soils generally. As stated above, the evidence is that montmorillonitic clay, when present, is most concentrated in the finest-grained fraction of the soil (0.3μ or less).

This is consistent with the well established fact that the lattice layers of montmorillonitic clay rarely exceed one micron in length and usually they are much smaller. On the other hand the crystals of kaolinite grow to larger size. For this reason the quantitative estimation of these clays is facilitated by subdividing the clay material into two or more fractions.

Although vast areas in the United States and other countries have not been investigated, it is already apparent that the distribution of the several kinds of clay, and therefore of the various kinds of cation-exchange material, forms a highly complex pattern. In general it can be said that strongly leached soils, such as the true podsoles of temperate and colder climates, and the lateritic types of tropical and subtropical zones, tend to be kaolinitic.

Grassland soils such as those on the Russian steppes, and similar soils in the United States and Canada tend to be montmorillonitic. Dryland soils are often found to contain relatively much hydrous mica-type of clay, but there appear to be many exceptions to these statements. For example, montmorillonitic clay is found in all types of climate and also in soils derived from a great variety of parent rocks. The same can be said of kaolinite. Hydrous mica is by no means confined to dry climates. It is an important constituent of many soil types from various parts of the humid area of the United States and Europe.

It should not be inferred that parent material and the conditions under which weathering has taken place have no relation to the formation of the different kinds of clay. To do so would almost certainly be erroneous. However, this is a special problem, which although interesting in itself and of significant bearing on soil processes, is not essential to an understanding of cation exchange. Therefore, the formation of the clays will not be discussed here.

Finally, it may be pointed out, the cation-exchange material of the soil is not merely finely comminuted igneous rock material. Rather it is one or another of a few products which have been formed by the weathering of igneous rocks at some previous time. This material is, therefore, a "new formation" in the sense Gedroiz (1922) used the term. How the clays may have been moved about from place to place, as in alluvial, glacial and wind-borne materials, and how one clay may have been converted into another are also problems beyond the scope of this monograph.

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